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# Wet-Process Phosphoric Acid Preparation and Utilization of the By-product Gypsum

By

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The preparation of phosphoric acid by a process using Makatea and Morocco varieties of rock phosphate has been studied. Investigations have also been made on the suitability of by-product gypsum samples obtained from these two rock phosphates and also of two commercial samples of by-product gypsum for the production of ammonium sulphate.

The target for the phosphatic fertilizers production in India by the end of 1965-66 has been fixed at 0.4 million ton  $P_2O_5$  per year, and this is very likely to be increased to one million by the end of 1970-71. A substantial portion of the additional phosphatic fertilizers is expected to be based on wet process phosphoric acid.

In the usual processes<sup>1-4</sup> of manufacturing this acid, rock phosphate is allowed to react with sulphuric acid in presence of recycle phosphoric acid and gypsum is obtained as a by-product. Since the quantity of gypsum is about 4.5 tons per ton of  $P_2O_5$  produced, its disposal is a major problem in the phosphoric acid industry. Usually this gypsum is not utilized; it is slurried with water and sent to disposal dumps. In some localities it is used for making building plasters; for example, the gypsum obtained by the Nissan process<sup>5</sup> in Japan is sold for making a plaster for which it is claimed to be very suitable. Recommendations have also been made for the manufacture of ammonium sulphate<sup>1</sup> from by-product gypsum by the Merseburg process involving reaction with ammonium carbonate, but so far there are only one or two small units where this process is employed. In the absence of indigenous sources of sulphur in India, the production of ammonium sulphate from by-product gypsum is an attractive proposition, because the sulphate radical is used twice; first, in the preparation of phosphoric acid from rock phosphate and second, in fixing ammonia as ammonium sulphate.

The present investigations were undertaken to study the various aspects of preparation of wet process phosphoric acid and the utilization of by-product gypsum

in the manufacture of ammonium sulphate. Particular emphasis was given on finding out the conditions for the production of most suitable gypsum for its subsequent reaction with ammonium carbonate. In the first place, experiments were carried out with Morocco and Makatea varieties of rock phosphate. The reaction characteristics of these samples with sulphuric acid and the reaction of the by-product gypsum with ammonium carbonate solution were studied. The particle sizes of gypsum and of calcium carbonate formed after reaction were determined. For a comparative study, experiments were also carried out with two commercial samples of by-product gypsum, obtained by the Prayon<sup>1</sup> and Nissan<sup>5</sup> processes respectively.

## Experimental Procedure

### Materials

Two varieties of rock phosphate were used—the Morocco and the Makatea phosphates (Table 1). A sample of by-product gypsum was obtained from the fertilizer factory at Alwaye\* employing the Prayon<sup>1</sup> process, while another from Japan produced by the Nissan<sup>5</sup> process was received through Messrs International Ore & Fertilizer, New Delhi, (Tables 2 & 3).

### Reaction of Rock Phosphate with Acid

The experimental set-up for the reaction is shown in Fig. 1. The Pyrex glass reaction vessel (B), a three-necked round bottom flask, is of 3 l. capacity. Its central

\* The Fertilizers & Chemicals Travancore Ltd., Udyogamandal, Kerala.



TABLE 1—CHEMICAL ANALYSIS OF ROCK PHOSPHATES, %

	<i>Makatea Variety</i>	<i>Morocco Variety</i>
SiO <sub>2</sub>	0.80	2.44
Fe <sub>2</sub> O <sub>3</sub> +Al <sub>2</sub> O <sub>3</sub>	4.06	2.93
CaO	48.98	48.26
MgO	0.15	0.37
P <sub>2</sub> O <sub>5</sub>	36.37	33.14
SO <sub>3</sub>	1.20	1.10
F	3.84	4.73
CO <sub>2</sub>	2.72	5.60
NaCl	0.01	0.10
Moisture	1.50	1.30
Alkali Oxides	0.37	0.03
Loss on Ignition	8.02	7.75

TABLE 2—CHEMICAL ANALYSIS OF GYPSUM SAMPLES, %  
(Dried at 45°C)

	<i>By-product Gypsum</i>				<i>Natural Gypsum</i>
	<i>Makatea</i>	<i>Morocco</i>	<i>Alwaye</i>	<i>Nissan</i>	<i>Pakistan</i>
SiO <sub>2</sub>	0.59	1.29	2.16	3.00	0.37
Fe <sub>2</sub> O <sub>3</sub> +Al <sub>2</sub> O <sub>3</sub>	1.30	0.40	0.40	0.82	0.14
CaO	33.04	32.36	34.23	31.94	31.81
MgO	0.10	0.04	0.03	Traces	0.66
F	1.01	1.45	2.29	1.23	—
P <sub>2</sub> O <sub>5</sub>	0.64	0.32	1.03	1.37	—
SO <sub>3</sub>	44.42	44.71	44.61	45.29	45.93

TABLE 3—SIZE ANALYSES OF GYPSUM AND CHALK

(Values represent Cumulative Wt. per cent above Particular Size Range)

	<i>Makatea</i>		<i>Morocco</i>		<i>Alwaye</i>		<i>Nissan</i>		<i>Pakistan</i>	
<i>Size</i>	<i>Gypsum</i>	<i>Chalk</i>	<i>Gypsum</i>	<i>Chalk</i>	<i>Gypsum</i>	<i>Chalk</i>	<i>Gypsum</i>	<i>Chalk</i>	<i>Gypsum</i>	<i>Chalk</i>
100 mesh B.S.S.	5.95	12.76	0.44	0.83	27.08	8.04	24.02	3.07	1.40	7.80
150 mesh B.S.S.	10.15	15.16	1.01	6.80	53.01	8.09	49.42	7.17	11.52	13.31
200 mesh B.S.S. (76 μ)	11.99	16.40	3.48	10.82	66.44	8.79	59.30	9.27	15.90	17.12
32.6 μ	17.01	17.10	8.51	74.12	73.74	80.36	83.11	60.94	78.30	44.34
22.8 μ	22.55	72.66	89.07	89.70	87.66	94.67	93.28	90.91	89.41	67.23
18.3 μ	64.10	90.67	93.70	92.93	90.50	96.35	95.46	92.82	97.24	89.23
12.2 μ	95.38	94.04	95.24	95.96	91.16	97.63	97.34	95.34	98.83	97.12
7.0 μ	96.28	95.47	95.50	97.57	95.26	98.62	97.83	96.63	99.00	98.50
4.0 μ	98.46	96.63	96.79	98.59	95.99	99.05	98.82	97.53	99.20	99.21

neck is closed by a rubber stopper through which is introduced a B19 socket coupled with a B19 cone, the other end of the cone being attached to the adapter of a sealed stirrer assembly. This assembly comprises one adapter, a chuck to hold the shaft of the glass stirrer and two conjugated V-pulleys. The two pulleys are connected with another motor-driven pulley, and there is an arrangement for varying the speed of the stirrer.

In all reactions, 75 g. rock phosphate (80 per cent passing through 100 mesh B.S.) was taken in the reaction vessel maintained at  $70^{\circ} \pm 0.5^{\circ}\text{C}$ . A desired quantity of phosphoric acid solution of predetermined P<sub>2</sub>O<sub>5</sub> content was then added and the contents stirred for 4-5 min. at 90 r.p.m. A desired quantity of dilute sulphuric acid was then added slowly with a little increase in the stirrer speed. After some time the stirrer speed was maintained at 90 r.p.m., and the reaction was allowed to proceed for a definite period. During the reaction, a suction of 12 mm. of water was maintained (Fig. 1).

After the reaction, the slurry was filtered under a vacuum of 20 in. of Hg. through a No. 1 Whatman filter paper, and the filtration time was noted. The filter cakes were washed with dilute phosphoric acid solutions and finally with distilled water. The strengths

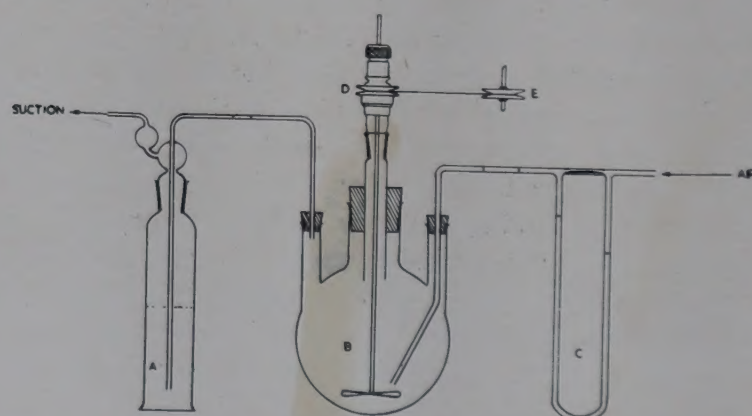


Fig. 1—Phosphoric Acid Reactor

A—Gas Scrubber  
B—Reaction Vessel  
C—Manometer  
D—Main Pulley  
E—Auxiliary Pulley



of acid solutions were so adjusted that during the first and second washings these were respectively about half and one-fourth of that of the acid originally added to the reaction mixture. All washings were done under the same suction as in the first filtration. The washed cakes were dried at 45°C and analysed.

#### Reaction of Gypsum with Ammonium Carbonate

The reactions of gypsum samples with ammonium carbonate were carried out according to the method developed earlier.<sup>6</sup> The quantity of gypsum taken in each experiment was smaller in the present series of experiments and the reaction vessel had smaller dimensions (Tables 4 & 5).

TABLE 4—BEHAVIOUR OF GYPSUM ON REACTION WITH AMMONIUM CARBONATE

Gypsum Samples	Filterability of Magma*	Conversion, %
Makatea	20	98.9
Morocco	19	98.8
Alwaye	32	98.7
Nissan	33	97.5
Pakistan	14	97.5

\* Expressed as average period (in sec.) for complete filtration.

TABLE 5—CHEMICAL ANALYSIS OF CHALK OBTAINED FROM BY-PRODUCT GYPSUM AFTER REACTION WITH AMMONIUM CARBONATE, %

(Results are Expressed on Dry Basis)

	Chalk Samples			
	Makatea	Morocco	Alwaye	Nissan
SiO <sub>2</sub>	0.88	2.03	3.32	3.95
Fe <sub>2</sub> O <sub>3</sub> +Al <sub>2</sub> O <sub>3</sub>	2.36	0.70	0.80	1.52
CaO	52.29	51.12	46.92	49.71
MgO	0.14	0.09	0.04	Traces
F	1.50	2.15	2.73	1.34
Total P <sub>2</sub> O <sub>5</sub>	0.86	0.58	1.41	0.61
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	2.21	3.45	3.32	3.30
CaSO <sub>4</sub>	0.87	1.48	1.58	0.75

#### Particle Size Analyses

In the sieve-range, wet-sieve analyses of gypsum and chalk samples were carried out, while the sub-sieve analyses were done by the Andreasen pipette method<sup>7</sup> at 35.5°±0.1°C. For gypsum samples, the suspending fluid was gypsum-saturated water while chalk-saturated water was employed for chalk samples.

## Results & Discussion

### Reaction of Rock Phosphate with Acid

The experiments were carried out as in the usual processes, viz. reacting rock phosphate with a mixture of sulphuric and phosphoric acids. The effect of altering the strength and quantity of phosphoric acid added to a definite quantity of rock phosphate, keeping the amount of sulphuric acid constant, is indicated (Table 6). It has been observed that the P<sub>2</sub>O<sub>5</sub> and fluorine contents in the gypsum cake were least when 240 ml. of phosphoric acid with 28.6 per cent P<sub>2</sub>O<sub>5</sub> was used. The filtration and washing characteristics of the gypsum cake were good in all experiments in which phosphoric acid with 22.1 to 28.6 per cent P<sub>2</sub>O<sub>5</sub> were employed. With 34.0 per cent P<sub>2</sub>O<sub>5</sub> phosphoric acid, the reaction was not satisfactory. The gypsum cake was, to some extent, sticky and more of residual P<sub>2</sub>O<sub>5</sub> was present in the washed variety. The rate of filtration of the reaction slurry was also slower than in those cases where phosphoric acid of lower concentration was used.

In the second set of experiments, the reaction characteristics of Morocco and Makatea varieties of rock phosphate have been studied varying the reaction time between 2 to 4 hr., other conditions remaining the same (Table 7). The strength and volume of phosphoric acid used were 28.0 per cent P<sub>2</sub>O<sub>5</sub> and 240 ml. respectively, since these were found satisfactory in the first series of experiments (Table 6). The quantity of sulphuric acid added was slightly more in the second set of experiments than in the first so that the sulphate content in the acid liquor was 2.0 to 2.3 in the former set as compared to 1.4 to 1.8 in the latter. The increase in sulphate content was found to reduce the amount of fluorine and P<sub>2</sub>O<sub>5</sub> in the gypsum cake.

The results indicate that a satisfactory reaction of Morocco and Makatea varieties of rock phosphate with acid can be carried out under the specified temperature and other conditions, if the time of reaction is kept at 4 hr. (Table 7). The filterability of the reaction slurry deteriorates progressively with decrease in the time to 3 and to 2 hr, and the residual fluorine and P<sub>2</sub>O<sub>5</sub> in gypsum also correspondingly increases. Comparing the reaction characteristics of the two varieties of rock phosphate when the reaction period was 4 hr. it is observed that the conversion efficiency was slightly better with Morocco phosphate than with the Makatea variety. Gypsum obtained from Morocco rock phosphate also had better filterability than that from Makatea phosphate, although the particle size distribution in the former was finer than in the latter (Table 3). This



TABLE 6—REACTION OF MAKATEA ROCK PHOSPHATE WITH ACID UNDER DIFFERENT CONDITIONS

[75 g. Rock Phosphate taken in each reaction; Temp—70°C; Time of Reaction—4 hr]

Sl. No.	Phosphoric Acid Added		Sulphuric Acid Added		Filtration Time of Slurry, Sec.	1st Filtrate-Pro-duced acid		1st Wash		2nd Wash		3rd Wash		Filter Cake Dried at 50°C	
	Strength, % $P_2O_5$	Volume, ml.	Strength, % $SO_3$	Volume, ml.		% $P_2O_5$ in Filtrate	% $P_2O_5$ in Filtrate	% $P_2O_5$ in Filtrate	% $P_2O_5$ in Filtrate	% $P_2O_5$ in Filtrate	% $P_2O_5$ in Filtrate	% $P_2O_5$ in Filtrate	% $P_2O_5$ in Filtrate	% $P_2O_5$	% F
1.	22.1	240	56.9	82	16	27.39	22.88	Cake washed with 11.02% $P_2O_5$ Acid	11.65	Cakes washed with 5.51% $P_2O_5$ Acid	1.23	Cake washed with distilled water	1.30	1.62	
2.	"	200	"	"	14	26.35	20.33		11.35		1.33		1.26	1.45	
3.	"	160	"	"	14	25.85	19.05		10.81		1.40		1.48	1.50	
4.	24.9	240	"	"	14	29.56	24.36	Cake washed with 12.45% $P_2O_5$ Acid	11.86	Cakes washed with 6.22% $P_2O_5$ Acid	1.20	Cake washed with distilled water	1.31	1.26	
5.	"	200	"	"	16	26.53	23.49		11.67		1.21		1.21	1.30	
6.	"	160	"	"	12	25.85	23.59		10.21		1.48		1.34	1.20	
7.	28.6	240	"	"	10	32.67	28.35	Cake washed with 14.29% $P_2O_5$ Acid	14.58	Cake washed with 7.14% $P_2O_5$ Acid	1.04	Cake washed with distilled water	1.01	1.02	
8.	"	200	"	"	16	31.56	28.85		14.38		1.14		1.24	1.18	
9.	"	160	"	"	16	31.10	28.51		15.22		1.26		1.18	1.03	
10.	34.0	240	"	"	20	37.61	34.90	Cake washed with 17% $P_2O_5$ Acid	18.70	Cake washed with 8.5% $P_2O_5$ Acid	1.93	Cake washed with distilled water	2.20	0.87	
11.	"	200	"	"	21	36.65	35.23		17.90		1.84		1.84	0.80	
12.	"	160	"	"	24	36.23	35.39		19.26		1.96		1.98	0.81	



TABLE 7—REACTION OF MOROCCO AND MAKATEA  
VARIETIES OF ROCK PHOSPHATE WITH ACID

(Rock phosphate—75 g.: sulphuric acid (57%  $\text{SO}_3$ )—85 ml.:  
Phosphoric Acid (28.0%  $\text{P}_2\text{O}_5$ )—240 ml.: Temp.—70°C)

Sl. No.	Rock Phosphate Sample	Time of Reaction, hr.	Filtration Time of slurry, sec.	Filter Cake, Washed Thrice and Dried at 50°C %	
				$\text{P}_2\text{O}_5$	F
1.	Makatea Variety	4	10	0.64	1.01
2.	"	3	12	0.81	1.23
3.	"	2	17	0.98	1.94
4.	Morocco Variety	4	22	0.32	1.45
5.	"	3	25	0.41	1.49
6.	"	2	31	0.82	2.02

may be attributed to the difference in the nature of impurities in the two varieties of rock phosphate. In an earlier publication<sup>6</sup>, it was pointed out that both particle size and impurities are important in determining the filterability of magmas and a small amount of impurities might seriously affect the filtration rates even though the general particle size distribution may be relatively coarse.

#### *Reaction of Gypsum Cake with Ammonium Carbonate*

The chemical composition of the gypsum gives only a broad indication of its possible use. The filterability of the magma is the most important factor in determining the suitability of a particular gypsum for reaction with ammonium carbonate solution. Hence, in order to study the utilization of by-product gypsum for the production of ammonium sulphate, four samples were allowed separately to react with ammonium carbonate and the reaction and filtration characteristics were determined. None of the samples was subjected to any treatment before reaction with ammonium carbonate. For the sake of comparison, a sample of natural gypsum from Pakistan was also allowed to react with ammonium carbonate under similar conditions (Table 4). The results indicate that although the conversion was good in all the cases, the filterability of magmas showed

appreciable variation when different gypsum samples were used. The filtration rate of magma from Pakistan gypsum was about 1.4 times that obtained from Morocco or Makatea by-product gypsum and about 2.3 times that from Alwaye or Nissan gypsum. Experience in Sindri factory over a period of several years has shown that Pakistan gypsum gives a magma that filters exceedingly well, and that plant operation is quite satisfactory even when the filtration rate of magmas is two-third of that from Pakistan gypsum. On this standpoint, the magmas from Morocco and Makatea gypsum may be classed as good-filtering while those from Alwaye and Nissan gypsum as medium-filtering. It will be observed that chalk samples have coarser size distribution than the original gypsum in cases of Morocco and Makatea samples, while reverse is the case with Alwaye and Nissan samples (Table 3). Thus, the two by-product gypsum samples produced from Morocco and Makatea varieties of rock phosphate in the present series of experiments appear to be better than the two commercial samples so far as the suitability for conversion to ammonium sulphate is concerned.

#### **Acknowledgements**

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# Separation of Water- and Citrate-Soluble Phosphates in Phosphatic Fertilizers by Paper Chromatography

By

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A new method for the separation of water and citrate-soluble phosphates in phosphatic fertilizers by paper chromatography has been developed. It consists of fixing the citrate-soluble phosphates by sodium carbonate, allowing the water-soluble phosphates to separate and the development of the chromatogram by using potassium ferrocyanide as the reducing agent.

The behaviour and availability of phosphate in soil play a very important role in stabilization of soil fertility and in influencing plant nutrition. The complex phenomenon of phosphate reversion from a water-soluble to citrate-soluble and insoluble states, taking place continuously in soil, has engaged the attention of soil scientists from early times.

The separation of inorganic ions in general and of phosphatic ions in particular by chromatographic techniques has been tried by a number of workers, including Ando<sup>1</sup>, whose method was a modification of that of Hanes and Isherwood<sup>2</sup> for detection of sugar phosphate; Westmann<sup>3</sup> and Bonnin<sup>4</sup> who introduced the use of stannous chloride as a substitute for benzidine in the spray reagent; Crowther<sup>5</sup> who substituted ultra-violet irradiation for the reducing solution resulting in deep blue spots for the phosphates; and Baumann<sup>6</sup> who introduced the procedure of prior hydrolysis of the chromatogram. The experimental techniques for the separation of inorganic phosphates from other ions were worked out by Karl-Kroupa<sup>7</sup> and Gauthier<sup>8</sup>. Sansoni and Baumgartner<sup>9</sup> advocated use of borate buffer of pH 10 for the separation of condensed phosphates by the technique of electrochromatography. However, the previous work<sup>10</sup> was mainly on the detection of phosphate radicle and the separation of polyphosphates into individual components by chromatographic techniques.

The separation of individual phosphates of mono and divalent metal ions, viz. those normally present in the soil, have not been tried earlier. Such phosphates include

diammonium hydrogen phosphate, ammonium dihydrogen phosphate, disodium hydrogen phosphate, sodium dihydrogen phosphate and calcium monophosphate, which are water-soluble; calcium diphosphate which is citrate-soluble and calcium triphosphate, iron and aluminium phosphates, which are insoluble. Amongst the water-soluble phosphates, calcium monophosphate is readily converted to dicalcium phosphate due to atmospheric carbon dioxide and alkalinity in soil and as such it is rarely found in soil. Chemical methods for the separation of these phosphates have been suggested from time to time but they are cumbersome and unreliable. It was, therefore, considered desirable to investigate the problem of separation of water-soluble and citrate-soluble phosphates in phosphatic fertilizers, and develop a chromatographic technique for their rapid separation.

## Experimental

The method consists of dissolving a mixture of inorganic water and citrate-soluble phosphates in the least amount of 2N hydrochloric acid, fixing the citrate-soluble phosphates by the interaction of sodium carbonate and allowing the water-soluble phosphates to develop using various mobile solvent phases, and finally developing the chromatogram by spraying a solution consisting of potassium ferrocyanide as the reducing agent in place of the usual benzidine solution. The former reduces the free molybdate to brown colour, leaving phospho-molybdate complex white on the paper chromatogram. Of all the paper chromatographic



techniques tried for the separation of these phosphates, viz. ascending, descending, circular and two dimensional flow techniques, the circular radial flow was found to be most suitable to effect a satisfactory separation. The ascending and descending techniques produced tailing of the spots on the chromatogram which were difficult to remove in neutral or alkaline solvent phases.

The reagents used were B.D.H. Analar or G.R.E. Merck, and a 0.5 per cent solution of ammonium phosphate, ammonium dihydrogen phosphate, sodium phosphate and sodium dihydrogen phosphate was prepared in double distilled water and made acidic with a few drops of 2N hydrochloric acid. 0.5 per cent solution of tricalcium phosphate and dicalcium phosphate were prepared by using the minimum possible amount of 2N hydrochloric acid required to keep the phosphates in solution while the total volume was made up with double distilled water. The solutions were freshly prepared to avoid changes taking place. Mixtures of these phosphates for analysis were obtained by mixing them in equal proportion v/v.

Whatman grade 1 chromatographic paper was used in all the experiments and the solvents used were of chromatographic grade. 26 cm. diam. papers were used for circular chromatography, while 2.5 cm. width strips were used for the ascending and descending chromatographic techniques. Chromatographic separations were carried out at room temp. in the tanks saturated with the vapours of the solvent.

One drop of the phosphate solution (individual phosphates and mixture of the phosphates taken separately) was applied at the centre of the circular paper and was allowed to dry. The spot was later made alkaline by the addition of preadjusted required amount of 5 per cent sodium carbonate solution directly over it. The paper was dried after addition of each drop to keep the phosphate confined to the centre of the paper. The fixing of the water insoluble phosphate by the help of sodium carbonate requires great care because the presence of

excess of sodium carbonate may give rise to the formation of soluble phosphates by ionic change with water insoluble calcium phosphates.

## Results & Discussion

A number of paper chromatograms were run using a variety of mobile solvent phases under the conditions stated above. Only the representative groups of solvents giving satisfactory separation have been included (Tables 1 & 2). The usual time taken for achieving the desired separation on chromatograms varied from 2 to 3 hr. The water-soluble and the citrate-soluble phosphates in a mixture were identified and separated by marked difference in  $R_f$  values (Table 1), these values of indi-

TABLE 1—SEPARATION OF WATER- AND CITRATE-SOLUBLE PHOSPHATES FROM A MIXTURE

Sl. No.	Mobile Solvent Phases, Ratios v/v	$R_f$ Value of Water-Soluble Phosphate	$R_f$ Value of Citrate-soluble Phosphates
1.	n-Propanol: Water: Acetone 60: 10: 30	0.45	0.10
2.	n-Butanol: Acetone: Water 50: 20: 30	0.44	0.32
3.	n-Amyl Alcohol: Acetone: Water 30: 50: 20	0.43	0.27
4.	Iso-Butanol: Acetone: Water 60: 30: 10	0.30	0.17
5.	Ethyl Acetate: Iso-Propanol: Water 30: 30: 40	0.82	0.05
6.	Ethyl Acetate: Ethanol: Water 30: 30: 40	0.98	0.05
7.	Ethyl Methyl Ketone: Ethanol: Water 20: 30: 50	0.90	0.05
8.	n-Amyl Alcohol: n-Butanol: Methanol: Water 30: 20: 20: 30	0.28	0.05
9.	n-Amyl Alcohol: n-Propanol: Water: Acetone 30: 30: 30: 20	0.27	0.07

TABLE 2— $R_f$  VALUES OF INDIVIDUAL PHOSPHATES

Sl. No.	Phosphates	Solvents*								
		No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7	No. 8	No. 9
1.	Ammonium dihydrogen phosphate	0.46	0.45	0.44	0.30	0.80	0.98	0.90	0.25	0.29
2.	Ammonium phosphate	0.44	0.40	0.45	0.28	0.83	0.96	0.88	0.28	0.30
3.	Sodium dihydrogen phosphate	0.48	0.50	0.40	0.32	0.82	0.99	0.93	0.27	0.31
4.	Sodium phosphate	0.44	0.44	0.42	0.33	0.85	1.00	0.91	0.24	0.27
5.	Dicalcium phosphate	0.12	0.32	0.25	0.19	0.03	0.05	0.03	0.04	0.10
6.	Tricalcium phosphate	0.10	0.30	0.27	0.18	0.06	0.04	0.04	0.06	0.08

\* Solvents are in the order as shown in Table 1



vidual phosphates having been determined earlier for comparison (Table 2). The citrate-soluble phosphates were confined to a ring or spot very near the centre while the water-soluble ones were obtained as a ring away from the centre and towards the periphery of the chromatogram.

The paper chromatograms were developed by the classical method using ammonium molybdate and benzidine solution resulting in the rapidly vanishing blue spots or rings for the phosphates in ammoniacal medium. This method was, however, found to be not very satisfactory as permanent chromatograms could not be obtained, and this technique of location of phosphate could not be used in acidic medium. A new method of development of chromatograms was therefore used based on the basic principle that phosphomolybdate complex is not reduced by potassium ferrocyanide, whereas free molybdate is turned brown showing a white band of phosphate on brown background colour of chromatogram. This method consisted of spraying the dried chromatogram with a 0.4 per cent solution of ammonium molybdate in 8 per cent nitric acid, heating at 80°C for 10 min., and finally treating the chromatogram in a dipping trough with a 1.0 per cent potassium ferrocyanide solution. The developed and dried chromatograms showed white stable rings for the phosphates and was found to be advantageous in acidic medium as well. The separation of water-soluble and citrate-soluble phosphates from a mixture by paper chromatography has been shown in Table 1.

This new technique is an improvement over the classical methods, and is very sensitive in detecting small

amounts of these phosphates. Its only disadvantage, lies in the fact that tailing effect, if any, cannot be detected due to the highly coloured background of the chromatogram. However, if effective separation takes place the phosphate rings on the chromatogram are sharp and stable.

#### Acknowledgement

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# Corrosion in Benzole Recovery Section in a Coke Oven Plant

By

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Corrosion of mild steel equipment in contact with creosote oil used for scrubbing benzole from the coke oven gas at Sindri has been studied. Treatment of debenzolized oil with an optimum amount of ammonia, followed by dehydration at 215°-220°C, has been found to reduce the corrosion to a low value.

Extensive corrosion of mild steel equipment, such as tubes, heat exchangers and pipes, has occurred in the benzole scrubbing and stripping section in the coke oven plant at Sindri. Corrosion has been found to be more pronounced at the hotter portion of the equipment and near the bends. The benzole is scrubbed from the coke oven gas by creosote oil at ambient temperature and is subsequently recovered by a stripping operation in which the oil is heated up to 145°C. In this coke oven plant an indirect system of ammonia recovery is employed.

Similar corrosion, to a greater or lesser extent, has also been observed in coke oven plants in other parts of the world. The extent of corrosion cannot readily be related to the conditions of the operation or any other factor which affects the stripping process. Cawley and Newall<sup>1</sup> state that corrosion is more frequent in plants using creosote oil. Corrosion seemed to occur only when ammonia was present in the coke oven gas.

The following generalizations may be made on the basis of findings in different coke oven plants: (1) The corrosive agents, whether coming from the gas or originally present in the wash oil, are carried by the wash oil in circulation; (2) Corrosion is more severe in those portions of the heat exchangers, preheaters and oil coolers which are at higher temperatures; (3) it is more severe where creosote oil is employed than in those cases in which gas oil is used; and (4) it occurs more frequently in plants employing the indirect system of ammonia recovery. The present investigations were undertaken to evolve suitable remedies for the corrosion in the Sindri coke oven plant.

## Experimental

*Weight-Loss Experiments:* Mild steel test coupons of size 5 × 2.6 × 0.3 cm. were used in the weight-loss experiments. A 6 mm. dia. hole was drilled in each of them. The coupons were cut out from mild steel sheets conforming to the specification—I.R.S.M. 16/49—and supplied by Messrs. Tata Iron & Steel Co. Ltd. Their surfaces were prepared by No. 0 emery paper, and the areas were measured accurately by callipers. They were then degreased in boiling toluene, washed with acetone, dried and weighed. After the experiments, the coupons were freed from the adhering tarry material by rubbing with cotton soaked in toluene and then treated with inhibited hydrochloric acid to remove corrosion products. The cleaning and drying processes were then repeated. They were weighed again. The loss in weight was expressed as mg./sq.dm./day.

The coupons were kept immersed in the oil by means of glass hooks passing through holes drilled in them. The experiments were carried out under reflux conditions at 170° ± 1°C for 8 hr. This temperature was selected to make the condition more drastic than in the plant where the maximum temperature of the oil is 145°C in the stripping column. For all these experiments, fresh creosote oil or debenzolized oil from the plant was used.

*Preparation of Aqueous Extracts of Debenzolized Oil:* The following procedure was used for the preparation of the aqueous extracts of the debenzolized oil: Debenzolized oil (100 ml.) and carbon tetrachloride (100 ml.) were mixed thoroughly and filtered. The residue was again extracted with carbon tetrachloride and filtered.



To the combined filtrate was added 200 ml. water, and to the residue a further 100 ml. of water was added. They were thoroughly shaken and left as such for 4 hr. The water layers were separated. Again 100 ml. water was added separately to the different fractions and the masses were shaken thoroughly. They were then allowed to stand for 4 hr. All the aqueous layers were then combined together and the acidity was determined by titration against standard alkali.

## Results & Discussion

The experimental results show that there is little corrosion of mild steel in fresh wash oil (obtained from Messrs Hindustan Steel Ltd.), whereas the debenzolized oil from the plants which has been in circulation for some time is quite corrosive (Table 1). It can be inferred from this that corrosive agents come mainly from the gas or are formed by the interaction of certain constituents in the gas with those present in wash oil. The experience in the plants is that the corrosive character of the wash oil increases with its time of circulation. Extensive work by Wilson<sup>2-4</sup> suggests that ammonium salts and tar acids are most probably responsible for the corrosion although hydroxy derivatives of some hydrocarbons also seem to play some part. Presence of water in the oil has an adverse effect since it helps in dissolving ammonia which forms an emulsion with the oil. Water also increases the corrosive effect of H<sub>2</sub>S which has been found to be non-corrosive in the absence of moisture. It may be noted that the coke oven gas coming from the benzole recovery section still contains hydrogen sulphide (1.0-1.6 g./NM<sup>3</sup>) and ammonia (19-33 g./NM<sup>3</sup>). The moisture can increase the corrosive effect in another way, viz. by dissolving

TABLE 1—CORROSION OF MILD STEEL IN WASH OIL  
(Temperature 170°±1°C; Duration of Test 8 hr.)

(Corrosion Rate expressed as mg/sq. dm/day)

Sl. No.	Fresh Wash Oil*	Corrosion in	
		Debenzolized Oil	
		As Received from Plant	Dehydrated
1.	7.1	—	—
2.	—	151.0	52.1
3.	—	110.4	67.1

\* Obtained from Hindustan Steel Ltd.

ammonium salts present in the oil. As is well-known, the solution of ammonium salts in water are corrosive to mild steel.

A study was, therefore, undertaken to see whether removal of water would reduce the corrosion. The oil was dehydrated by keeping it at 215°-220°C and it was observed that the corrosion rate was thereby reduced considerably (Table 1). The dehydration treatment was also effective in decomposing ammonium thiocyanate which has been reported to be mainly responsible for corrosion by wash oil<sup>3-6</sup>.

It was further observed that the aqueous extracts of debenzolized oil were acidic. Hence the corrosive character of the debenzolized oil was also studied after neutralization with ammonia or sodium hydroxide with or without subsequent dehydration. The results show that neutralization lowers the corrosivity and the effect is enhanced by dehydration (Table 2). There seemed to be an optimum amount of ammonia with

TABLE 2—EFFECT OF NEUTRALIZATION AND DEHYDRATION ON THE CORROSION OF MILD STEEL IN DEBENZOLIZED OIL

(Temperature—170°±1°C; Duration of Test—8 hr.)

(Corrosion Rate expressed as mg./sq.dm./day)

Sl. No.	Debenzolized Oil	Corrosion Rate after Neutralization											
		NH <sub>3</sub> , 8.66 g./l.						NaOH, 0.4 g./l.					
		Without Dehydration						Followed by Dehydration					
		NH <sub>3</sub> , 8.66 g./l.	NH <sub>3</sub> , 17.32 g./l.	NH <sub>3</sub> , 20.79 g./l.	NH <sub>3</sub> , 24.25 g./l.	NH <sub>3</sub> , 34.65 g./l.	Without Dehydration	NaOH, 0.4 g./l.	NaOH, 0.8 g./l.	NaOH, 0.96 g./l.	NaOH, 1.2 g./l.	NaOH, 1.6 g./l.	NaOH, 1.6 g./l.
1.	Sample No. 1 (Corrosion rate 151.0 mg/sq.dm/day)	82.9	36.1				90.2	28.9					
2.	Sample No. 2 (Corrosion rate 110.4 mg/sq.dm/day)	—	—	19.2	39.3	55.2	60.4	—	—	15.0	30.9	46.1	47.7



TABLE 3—EFFECT OF NEUTRALIZATION AND DEHYDRATION ON THE CORROSION OF MILD STEEL  
IN DEBENZOLIZED OIL

(Temperature  $170^{\circ} \pm 1^{\circ}\text{C}$ ; Duration of Test—8 hr.)

Sl. No.	Acidity of Aqueous Extract from 1 l. of Oil (as equivalent $\text{NH}_3$ in g.)	In As- Received Oil	Corrosion Rate, mg./sq. dm./day										
			After Treatment with Different Quantities of Ammonia Followed by Dehydration at $215^{\circ}\text{--}220^{\circ}\text{C}$										
			$\text{NH}_3$ , 0.236 g./l.	$\text{NH}_3$ , 0.472 g./l.	$\text{NH}_3$ , 0.531 g./l.	$\text{NH}_3$ , 0.606 g./l.	$\text{NH}_3$ , 0.708 g./l.	$\text{NH}_3$ , 0.709 g./l.	$\text{NH}_3$ , 0.787 g./l.	$\text{NH}_3$ , 0.886 g./l.	$\text{NH}_3$ , 0.944 g./l.	$\text{NH}_3$ , 1.179 g./l.	$\text{NH}_3$ , 2.338 g./l.
1.	0.354	121.5	35.9	13.1	—	—	8.1	—	—	—	35.2	39.1	50.3
2.	0.354	106.4	—	—	29.1	—	—	11.2	—	33.6	—	—	—
3.	0.360	118.1	—	—	—	31.5	—	—	12.6	—	32.3	—	—

which the debenzolized wash oil was to be treated so that the corrosion of mild steel was reduced to the minimum.

Further experiments were carried out to arrive at such an optimum amount of ammonia. Aqueous extracts of 1 l. of debenzolized oil were prepared by the method already described, and they were then treated with different quantities of ammonia. In separate experiments, rates of corrosion of mild steel in debenzolized oil were determined after addition of different quantities of ammonia and then by dehydration at  $215^{\circ}\text{--}220^{\circ}\text{C}$ . The results show that the optimum amount of ammonia that should be added to a definite volume of debenzolized oil is double the quantity required to neutralize the aqueous extract obtained from the oil (Table 3).

The feasibility of using an alternative material of construction was also examined. It was found that the corrosion rate of an aluminium alloy (M27S; containing

2 per cent magnesium) in debenzolized oil was of the order of 1 mg./sq. dm./day—an extremely low value. Thus, the use of this alloy may also be considered as a solution to the problem of corrosion of plant equipment by wash oil.

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# Efficiency of Various Forms of Phosphate in Crop Plant Nutrition

## PART II—RESPONSE OF *AMAN* PADDY IN FIELD TRIALS

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Performance of multiphosphate, fused calcium magnesium phosphate, calcined phosphate and superphosphate under water-logged field conditions has been studied using *aman* paddy as the test crop. Multiphosphate treatments resulted in higher grain and straw yields of *aman* paddy than the corresponding three other fertilizer treatments.

### Introduction

In the previous pot culture experiment<sup>1</sup> with *aus* paddy it was observed that multiphosphate treated plants produced higher dry matter yields and utilized more phosphorus than in the case of superphosphate, fused calcium magnesium phosphate and calcined phosphate treated plants. The present investigation was undertaken to confirm the above findings under normal water-logged field conditions using *aman* paddy as the test crop.

### Experimental

The field experiment was conducted in the Fertilizer Trials Station of this Division at Sindri. The experimental plot was fairly uniform in fertility slope, drainage, etc. (Table 1). The land was ploughed in June

without any break with a disc plough, the headland being kept outside the experimental area. It was then finely puddled. Patnai-23 variety of *aman* paddy, which responds very well to phosphatic fertilizer treatments, was selected for this trial. Japanese method<sup>2</sup> of seed selection, seed bed preparation and sowing was followed with the exception that no fertilizer was applied to the seed beds.

The fertilizers which were tested in the previous pot culture experiment<sup>1</sup> viz. Multiphosphate, superphosphate, fused calcium magnesium phosphate and calcined phosphate were applied at the rate of 25, 50 and 100 lbs. of  $P_2O_5$  per acre, immediately before transplanting. Micro plot technique developed in Rothamsted<sup>3</sup> was followed, the effective plot area being  $\frac{1}{94.6 \times 9}$  th of an acre. The row to row and plant to plant distances were 12" and 8" respectively. 5 weeks old seedlings were transplanted on 5.8.64, three seedlings being put per hill. The fertilizers were puddled thoroughly with the soil immediately before transplanting, and total amounts applied were as below (Table 2).

Sufficient care was taken to maintain a steady level of water in the various plots. Two weeding operations were performed on 4.9.64 and 19.9.64 respectively. In order to control the attack of stem borers, 0.03 per cent soln. of Folidol-E605 was sprayed on 10.10.64. Regular growth measurements were made, the results being recorded in terms of rate of increase in height, number of increase of tillers, length of panicles etc. For determining the nutrient contents of the plants and soils the previous methods were used. Finally, the crop was harvested on 17.12.64.

TABLE 1—ANALYSIS OF SOIL SAMPLES (ON OVEN DRY BASIS)

(A) Mechanical Analysis, %	
Clay	27.95
Silt	21.22
Sand	45.95
(B) Chemical Analysis	
Organic Carbon, %	1.211
Total Nitrogen, %	0.154
Total $P_2O_5$ , %	0.185
Total $K_2O$ , %	0.941
pH	8.4
Base Exchange Capacity, m.eq./100 g. soil.	24.151
Exchangeable bases, m.eq./100 g. soil.	
(a) Exchangeable $K^+$	0.361
(b) Exchangeable $Na^+$	1.176



TABLE 2—APPLICATION OF FERTILIZERS IN THE SOIL

No.	Abbreviations	Phosphatic Fertilizer	Lbs/acre of $P_2O_5$	Amount of fertilizer per plot g.
1.	Control	—	0	0
2.	C <sub>1</sub>	Multiphosphate	25	89.81
3.	C <sub>2</sub>	Multiphosphate	50	179.62
4.	C <sub>3</sub>	Multiphosphate	100	359.25
5.	M <sub>1</sub>	Calcined phosphate	25	65.99
6.	M <sub>2</sub>	Calcined phosphate	50	131.99
7.	M <sub>3</sub>	Calcined phosphate	100	263.99
8.	F <sub>1</sub>	Fused phosphate	25	118.16
9.	F <sub>2</sub>	Fused phosphate	50	236.32
10.	F <sub>3</sub>	Fused phosphate	100	472.65
11.	S <sub>1</sub>	Superphosphate	25	144.58
12.	S <sub>2</sub>	Superphosphate	50	289.17
13.	S <sub>3</sub>	Superphosphate	100	478.34

## Results and Discussion

*Effect of Fertilizers on Growth and Development of Rice Plants:* Height measurement results indicated that at all the three levels, multiphosphate-treated plants were the tallest followed by those treated with superphosphate, fused phosphate and calcined phosphate (Table 3). The differences in the rate of growth following the various fertilizer treatments were perceptible throughout the growing season. In all the treatments, the third level ones produced the tallest plants followed by the second and first level ones.

As it is quite apparent from Figs. 1 and 2 (Table 4), multiphosphate-treated plants produced higher number of tillers (total and effective), longer panicles (Fig. 3, Table 5) and more number of grains per panicle (Fig. 4, Table 6), followed by those treated with superphos-

phate, calcined phosphate and fused phosphate. Third level-treated plants were superior in these respects followed by the 2nd, 1st and control plants.

*Yield of Rice Straw and Grains:* At the 5 per cent level of significance, the statistical interpretations of the results are as follows:

### STRAW:

C<sub>3</sub> S<sub>3</sub> F<sub>3</sub> M<sub>3</sub> S<sub>2</sub> C<sub>2</sub> C<sub>1</sub> F<sub>2</sub> M<sub>2</sub> S<sub>1</sub> M<sub>1</sub> F<sub>1</sub> Control

### GRAIN:

C<sub>3</sub> S<sub>3</sub> M<sub>3</sub> F<sub>3</sub> S<sub>2</sub> C<sub>2</sub> F<sub>2</sub> M<sub>2</sub> C<sub>1</sub> S<sub>1</sub> M<sub>1</sub> F<sub>1</sub> Control

The straw yield of the C<sub>3</sub> treated plants was respectively 5.44, 10.71, 11.51 and 65.47 per cent above those of S<sub>3</sub>, F<sub>3</sub>, M<sub>3</sub> and control plants. In C<sub>2</sub> plants, values were 10.43, 12.90 and 37.33 per cent greater than those of the F<sub>2</sub>, M<sub>2</sub> and control plants respectively.

In the case of grain yields, C<sub>3</sub> plants produced respectively 10.18, 13.35, 13.35 and 45.12 per cent higher yields than S<sub>3</sub>, M<sub>3</sub>, F<sub>3</sub> and control plants. C<sub>2</sub> plants produced 7.44, 8.62 and 23.17 per cent higher grain yields above those of F<sub>2</sub>, M<sub>2</sub> and control plants. In C<sub>1</sub> plants values were 2.20, 6.91, 9.43 and 13.41 per cent greater than those of the S<sub>1</sub>, M<sub>1</sub>, F<sub>1</sub> and control plants.

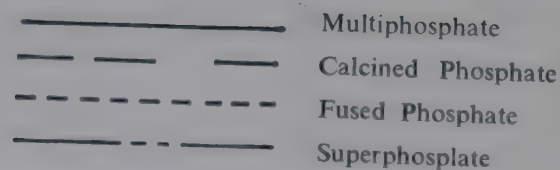
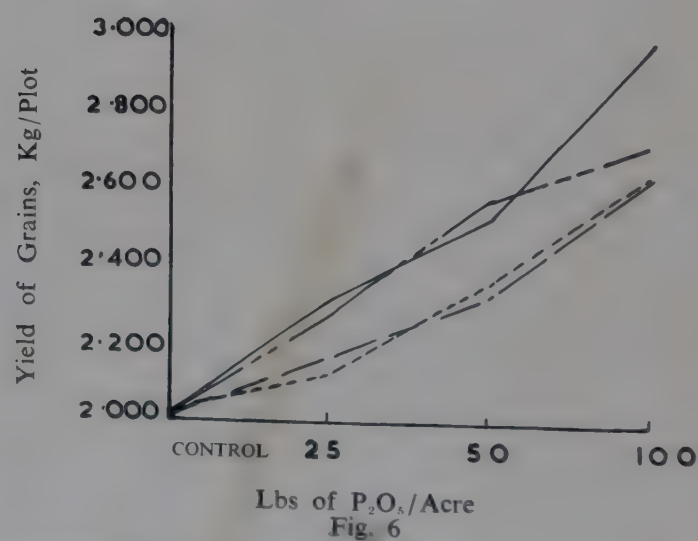
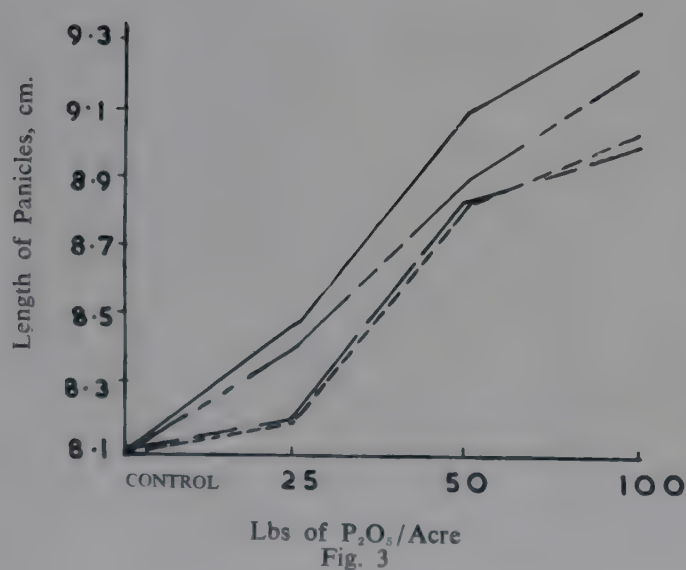
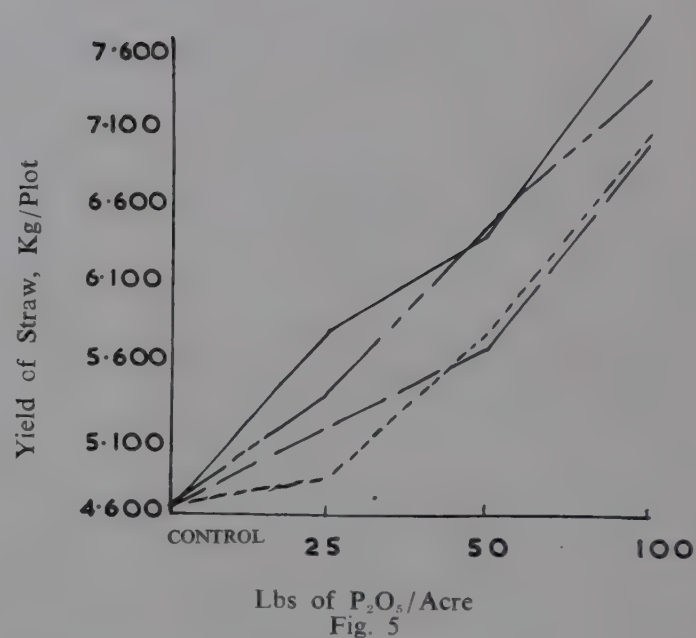
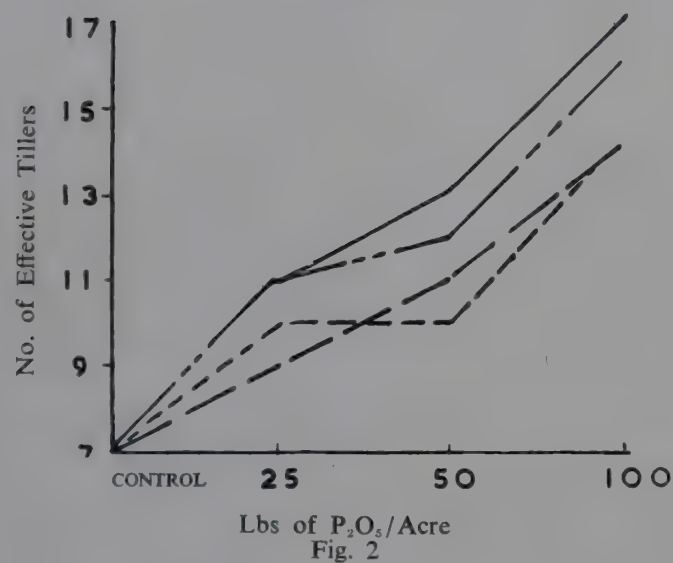
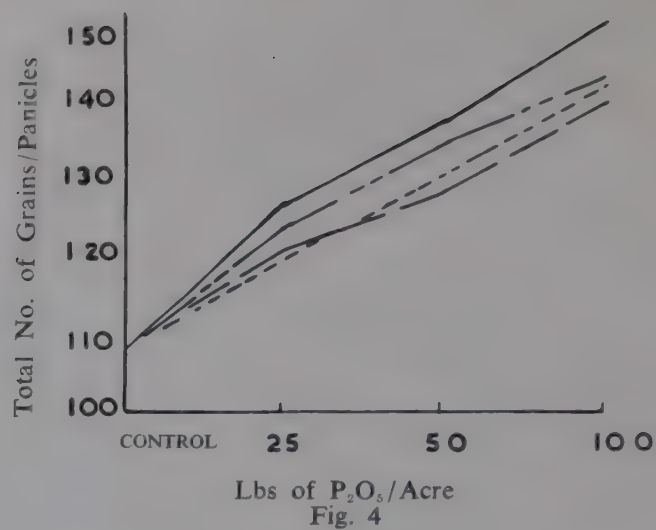
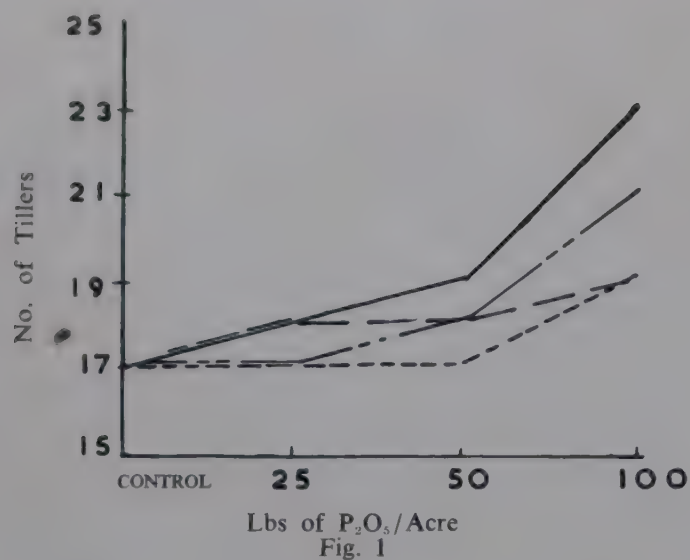
*Uptake of Nitrogen by the Rice Plants:* It is clear from Figs. 7 & 8 (Table 7, columns 2 and 4) that at all the three levels of phosphate application—except the S<sub>3</sub>-treated rice grains—superphosphate-treated plants took

TABLE 3—HEIGHTS OF RICE PLANTS ON DIFFERENT DATES (cm.)

(Each figure represents an average of eight measurements)

Treatments	21.8.64	28.8.64	4.9.64	11.9.64	18.9.64	25.9.64	2.10.64	9.10.64	16.10.64	23.10.64	30.10.64
Control	40	51	54	60	65	80	98	107	111	122	131
C <sub>1</sub>	42	53	56	65	69	89	104	110	123	133	141
C <sub>2</sub>	42	55	59	68	77	93	107	116	128	138	149
C <sub>3</sub>	43	57	63	72	80	95	112	120	132	142	155
M <sub>1</sub>	40	51	53	61	67	84	101	107	120	125	134
M <sub>2</sub>	40	51	53	63	69	86	103	109	121	127	139
M <sub>3</sub>	41	52	58	67	72	87	106	110	123	131	144
F <sub>1</sub>	40	50	53	62	66	83	101	108	120	126	134
F <sub>2</sub>	41	51	53	63	69	85	102	119	120	128	140
F <sub>3</sub>	41	53	57	68	73	87	105	111	122	130	147
S <sub>1</sub>	41	51	55	63	68	86	103	111	122	129	137
S <sub>2</sub>	40	53	59	65	75	88	105	113	124	130	145
S <sub>3</sub>	42	55	61	70	78	91	109	118	128	136	150







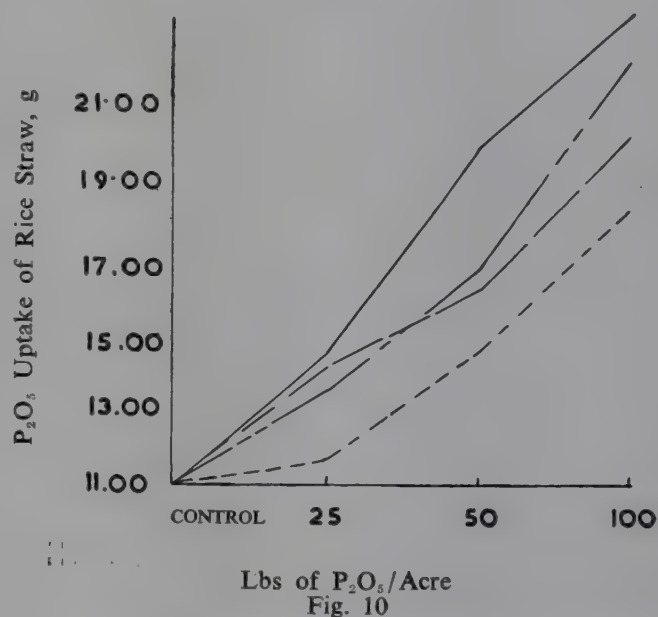
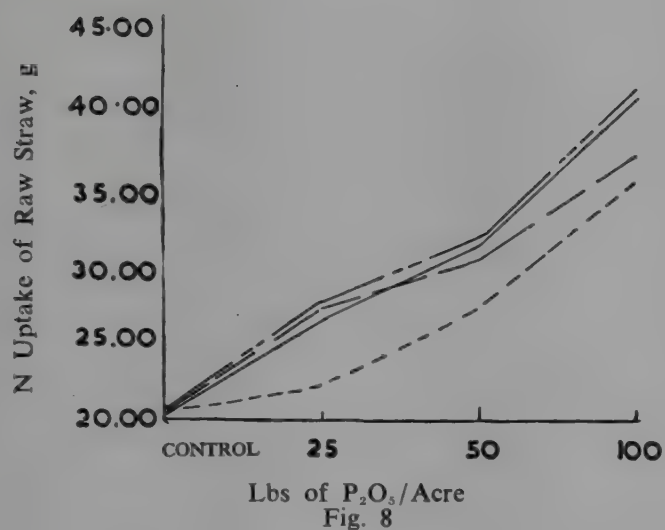
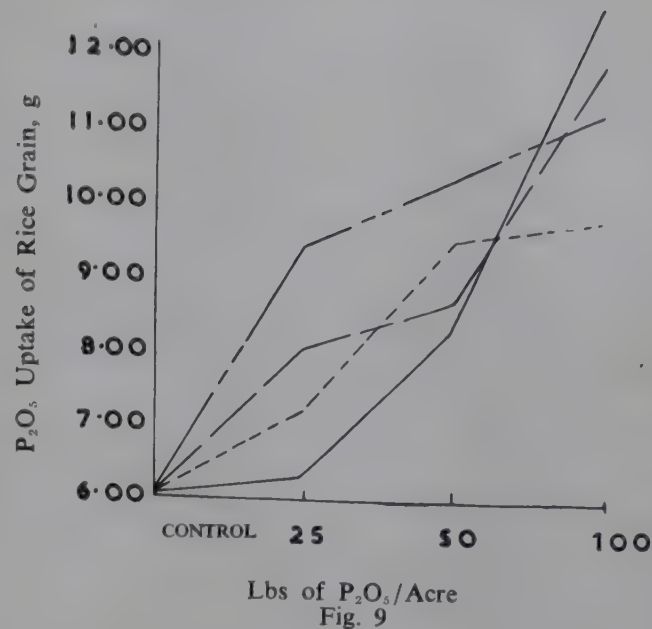
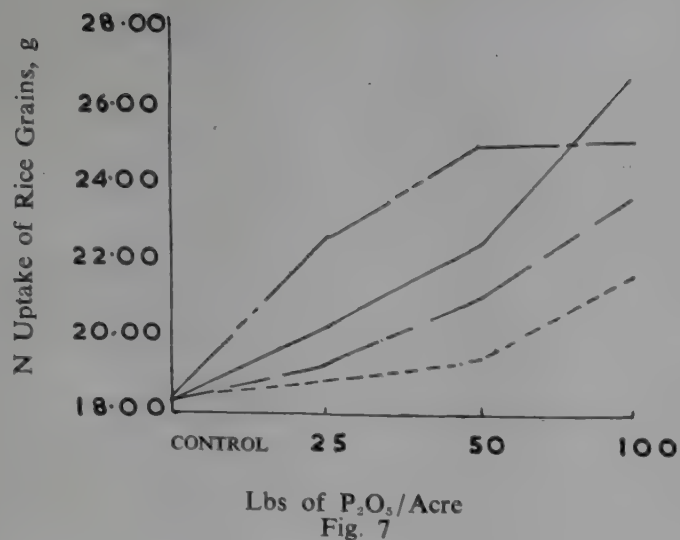


TABLE 4—TILLERS OF RICE PLANTS

(Each figure represents an average of eight counts)

Treatments	Number of Tillers against Dates						Effective tillers
	21.8.64	28.8.64	4.9.64	11.9.64	18.9.64	25.9.64	
Control	5	5	8	10	15	17	7
C <sub>1</sub>	5	5	9	14	17	18	11
C <sub>2</sub>	6	7	11	15	19	19	13
C <sub>3</sub>	6	7	13	16	22	23	17
M <sub>1</sub>	5	5	8	11	15	18	9
M <sub>2</sub>	5	6	9	13	16	18	11
M <sub>3</sub>	5	6	9	13	17	19	14
F <sub>1</sub>	5	5	8	9	14	17	10
F <sub>2</sub>	6	5	9	11	14	17	10
F <sub>3</sub>	6	6	9	12	16	19	14
S <sub>1</sub>	5	5	9	12	15	17	11
S <sub>2</sub>	5	6	10	13	17	18	12
S <sub>3</sub>	6	7	12	14	20	21	16

TABLE 5—LENGTH OF PANICLES, GRAINS PER PANICLE AND THOUSAND GRAIN WEIGHTS

(Each figure represents an average of eight sample clumps)

Treatments	Length of Panicles, cm.	No. of Grains/Panicle		Thousand Grain Weight, g.
		Total	Filled	
Control	8.10	108	97	29.70
C <sub>1</sub>	8.50	126	114	30.90
C <sub>2</sub>	9.10	136	124	29.00
C <sub>3</sub>	9.40	148	138	30.80
M <sub>1</sub>	8.27	120	113	29.70
M <sub>2</sub>	8.83	127	117	30.40
M <sub>3</sub>	9.00	138	130	29.70
F <sub>1</sub>	8.20	119	110	30.40
F <sub>2</sub>	8.80	129	117	29.70
F <sub>3</sub>	9.05	140	129	30.00
S <sub>1</sub>	8.41	123	113	29.80
S <sub>2</sub>	8.90	133	123	29.50
S <sub>3</sub>	9.26	141	133	29.70



TABLE 6—MEAN STRAW AND GRAIN YIELDS OF  
RICE PLANTS, KG./PLOT

Treatments	Rice Straw	Rice Grains
Control	4.625	2.050
C <sub>1</sub>	5.750	2.325
C <sub>2</sub>	6.350	2.525
C <sub>3</sub>	7.750	2.975
M <sub>1</sub>	5.125	2.175
M <sub>2</sub>	5.625	2.325
M <sub>3</sub>	6.950	2.625
F <sub>1</sub>	4.875	2.125
F <sub>2</sub>	5.750	2.350
F <sub>3</sub>	7.000	2.625
S <sub>1</sub>	5.375	2.275
S <sub>2</sub>	6.375	2.550
S <sub>3</sub>	7.350	2.700
'F' value of the treatments	65.34***	91.53***
C.D. at the 5% level	0.372	.084

\*\*\* Significant at the 0.1 % level.

TABLE 7—UPTAKE OF NUTRIENTS BY THE RICE PLANTS, g.

Treatments	Rice Grains		Rice Straw	
	N	P <sub>2</sub> O <sub>5</sub>	N	P <sub>2</sub> O <sub>5</sub>
Control	18.183	6.065	20.350	11.100
C <sub>1</sub>	20.181	6.277	26.450	14.375
C <sub>2</sub>	22.397	8.837	31.125	19.685
C <sub>3</sub>	26.775	12.495	40.812	23.312
M <sub>1</sub>	19.292	8.047	27.521	14.094
M <sub>2</sub>	20.925	8.602	30.312	16.062
M <sub>3</sub>	23.625	11.812	37.321	19.946
F <sub>1</sub>	18.849	7.225	21.937	11.700
F <sub>2</sub>	19.387	9.400	27.312	14.375
F <sub>3</sub>	21.656	9.712	35.000	18.200
S <sub>1</sub>	22.454	9.327	27.412	13.437
S <sub>2</sub>	24.990	10.200	31.875	16.575
S <sub>3</sub>	25.075	11.070	41.160	22.050

up higher quantities of nitrogen followed closely by multiphosphate, calcined phosphate and fused phosphate-treated ones.

Multiphosphate-treated rice straws, however, took up higher quantities of phosphate at all the three levels of phosphate application, followed by superphosphate, calcined phosphate and fused phosphate-treated rice straws. At the third level of phosphate application, the uptake of phosphate in the rice grains was of the order  $M_3 > C_3 > S_3 > F_3$ . At the second level it was  $S_2 > F_2 > C_2 > M_2$ , and at the first level it was  $S_1 > C_1 > F_1 > M_1$ . Control plants had the lowest values in all respects.

Higher uptakes of phosphate by the multiphosphate-treated rice straws explain the vigorous vegetative growth observed during the early stage of growth.

### Acknowledgements

The author's thanks are due to Dr. K. R. Chakravorty, General Manager, and Sri A. K. Roy, Deputy Superintendent, for their interest in this work. Thanks are also due to Sarbasri P. K. Chakravorty, B. N. Singh, B. Chowdhury and S. Roy and Sm. B. Bhowmik for their timely help.

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# Studies on Some Indian Limestones

## Part I: Mineralogical Investigation

By

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An attempt has been made to investigate the mineralogical composition of some Indian limestones by x-ray diffraction and differential thermal analyses. The cell constants of calcite, which is the major phase of these samples, have been calculated precisely and found to be somewhat different from the standard value of pure calcite except in the case of one variety. This difference has been attributed to the impregnation of magnesium carbonate in the calcite lattice. It has also been found from DTA that the peak temperature of such calcite is lower than that having no such impregnation. Again, dolomite has been found in all samples which contain this impregnated calcite.

### Introduction

Limestone rocks have often been found to be associated with dolomite. Geologists believe that such dolomitized limestone rocks are favourable for the deposition of other minerals. Due to such association of dolomite with other minerals a study of dolomitic limestone might help in exploring the location of such deposits. Besides, the dolomitized limestone has important industrial and agronomical uses. Limestone is used as diluent in the manufacture of calcium ammonium nitrate (CAN), and its association with dolomite is beneficial for the following reasons: (i) dolomite, being carrier of magnesium, is a plant nutrient, and (ii) has much less tendency to react with ammonium nitrate.<sup>1</sup>

In view of the above, it was proposed to attempt the x-ray diffraction as well as DTA techniques to identify the different phases present in some Indian limestones with particular reference to dolomite, and study the structural characteristics of their calcite.

### Experimental

#### Materials

Six different limestone and one dolomite samples, collected from the Nangal and Rourkela fertilizer factories, were used for the present investigation. The materials were finely ground, dried and stored in a desiccator.

#### X-ray Diffraction Analysis

All the limestone and dolomite samples were studied in the Philips x-ray diffractometer PW 1050/51 using nickel filtered  $\text{CuK}\alpha$  radiation and Geiger counter as detector. The x-ray tube was kept at 40 KV and 20 mA. Diffraction angles were obtained from charts recorded at a scanning speed  $1^\circ/\text{min}$ . with time constant 2 secs. A standard silicon, supplied by Philips, was also studied in order to correct the observed d-values, if any.

The complete set of samples examined with diffractometer was also studied in the Philips PW 1010 X-ray diffraction unit using nickel filtered  $\text{CuK}\alpha$  radiation and 114.6 mm. Philips camera in order to obtain an independent check.

In order to detect the impurities, all the samples were washed with acetic acid and X-ray photographs were taken. The cell constants  $a_0$  and  $c_0$  were calculated from the reflections  $d_{213}(140)$  and  $d_{444}(00.12)$ .

#### Differential Thermal Analysis

The Linseis model of DTA apparatus, designed to carry out analysis of three samples at a time, was used. Thermocouple used was of platinum and platinum-rhodium, and sample holders were of thin platinum cylinder having diameter and length as 0.7 and 2.5 cm. respectively. The rate of temperature rise was  $10^\circ\text{C}/\text{min}$ , which was controlled by a programme controller. The curves were recorded automatically.  $\alpha$  alumina



was used as a reference substance. It has been reported that the peak temperature of calcite varies from 860° to 1010°C due to the use of different apparatus, techniques, concentration of calcite in the sample, particle and crystal sizes.<sup>2</sup> It was observed that the crystalline nature of the samples used was similar, and DTA was performed under identical conditions in order to eliminate the effect that may arise due to the above variables.

## Results

The x-ray diffractions and DTA results are given in the Tables 1, 2 and 3. DTA diagrams are shown in Fig. 1.

TABLE 1—PHASES IDENTIFIED BY X-RAY AND DTA TECHNIQUES

Mineral	Major Phase		Minor Phases	
	X-ray	DTA	X-ray	DTA
Jharbada Limestone	Calcite	Calcite	Quartz	Pyrite
Monda Limestone	Calcite	Calcite	Dolomite & Quartz	Dolomite
Dabla Limestone	Calcite	Calcite	Dolomite & Quartz	Dolomite
Punjab Limestone	Calcite	Calcite	Dolomite & Quartz	Dolomite
Bisra Limestone	Calcite	Calcite	Dolomite & Quartz	Fine grained FeCO <sub>3</sub>
Purnapani Limestone	Calcite	Calcite	Dolomite & Quartz	Dolomite & Pyrite
Rishikesh Dolomite	Dolomite	Dolomite	Quartz	—

TABLE 2—LATTICE PARAMETER MEASUREMENTS OF THE SAMPLES

Mineral	$d_{211}(104)$	$a_0$	$c_0$	$c_0/a_0$	MgCO <sub>3</sub> from Goldsmith's Data <sup>3</sup> , %
Jharbada Limestone	3.035	4.989	17.058	3.447	Nil
Monda Limestone	3.0314	4.983	17.034	3.619	1
Dabla Limestone	3.0314	4.983	17.034	3.619	1
Punjab Limestone	3.0314	4.983	17.034	3.619	1
Bisra Limestone	3.0314	4.983	17.034	3.619	1
Purnapani Limestone	3.0314	4.983	17.034	3.619	1
Rishikesh Dolomite	2.884	4.811	16.038	3.333	—



Fig. 1—DTA Curves of Limestone Samples

TABLE 3—TEMPERATURE (°C) AND INTENSITY OF PEAK OF SAMPLES

Sample	Endothermic	Exothermic
Jharbada Limestone	110 weak bulge 1000 strong.	380 weak bulge
Monda Limestone	110 weak bulge 810 weak 970 strong	
Dabla Limestone	110 weak bulge 810 weak 970 strong	
Punjab Limestone	110 weak bulge 800 weak 970 strong	
Bisra Limestone	110 weak bulge 500 weak 810 weak 980 strong	550 weak
Purnapani Limestone	110 weak bulge 810 weak 970 strong	380 weak bulge
Rishikesh Dolomite	110 weak bulge 800 strong 960 strong	



It can be seen from the results (Tables 1 and 3 and Fig. 1) that all the limestone samples, except the Jharbeda variety, contain dolomite as one of the minor phases. The other minor phases present, as revealed by x-ray and DTA studies, are quartz in all the samples, pyrites in the Jharbeda and Purnapani varieties and fine grained  $\text{FeCO}_3$  (chalybite) in the Bisra variety.

## Discussion

It has been reported that  $\text{Mg}^{+2}$  can substitute for  $\text{Ca}^{+2}$  in calcite and high temperature will be needed to accomodate considerable amount of Mg in the calcite structure<sup>4,5</sup>. As a result of the solid solution formation between calcium carbonate and magnesium carbonate, an anisotropic lattice contraction occurs, and there will be shifts in the position of certain reflections both with a strong a—axis and c—axis components.  $\text{Fe}^{+2}$  will also act in the same way. Since the amount of substitution is generally very small in the naturally-occurring calcite, the magnitude of the shift in the peak position will be very small. Previous studies<sup>6</sup> have shown that the amounts of magnesium carbonate in the four weight per cent ranges occur generally in solution in calcite. It has also been reported by Faust<sup>7</sup> that calcite does not occur in nature with magnesite, although one of these minerals can exist in equilibrium with dolomite.

The cell constants of calcite have been determined accurately by a number of workers<sup>8</sup>. At 20°C,  $a_0 = 4.9900 \text{ \AA}$  and  $c_0 = 17.0615 \text{ \AA}$ . From the thermal expansion data of Austin et al<sup>9</sup>, the values of 26°C are  $a_0 = 4.9899 \text{ \AA}$  and  $c_0 = 17.064 \text{ \AA}$ . The values<sup>10</sup> for dolomite are  $a_0 = 4.8114 \text{ \AA}$  and  $c_0 = 16.039 \text{ \AA}$ , and for magnesium carbonate  $a_0 = 4.6330 \text{ \AA}$  and  $c_0 = 15.016 \text{ \AA}$ .

It can be seen that there is lattice variation in all the samples, except the Jharbeda variety, from that of the pure calcite, which may be due to magnesium carbonate (Table 2). From Goldsmith's<sup>3</sup> data on magnesium carbonate and the lattice parameter determined, the  $\text{MgCO}_3$  content of each limestone sample was obtained (Table 2). Only the Jharbeda variety seems

to be pure calcite, whereas the remaining limestones contain nearly one weight per cent of magnesium carbonate.

The cell constants of dolomite (Rishikesh variety) compares very well with those values of pure dolomite.

It is worthwhile to point out that in the DTA thermogram of limestone samples, the peak temperature of calcite is within the range 970°-980°C, except in the case of the Jharbeda variety (mainly calcite) where it is 1000°C. One of the causes for this deviation can be attributed to the impregnation of magnesium carbonate in the calcite lattice.

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# Design of Shift Reactor

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Individual rate coefficients for surface reaction and gas phase mass transfer in Shift reaction have been calculated from the published kinetic data, and these have been plotted in suitable graphs for rapid calculation of the overall rate of reaction. A simplified design procedure based on the use of these graphs has been suggested.

## Introduction

The solution of the design material and heat balance equations for finding an elemental volume of a shift reaction catalyst bed with a given small increase in gas temperature, and the conversion corresponding to this small increase in gas temperature requires evaluation of the overall rate of reaction at the conditions pertaining to the elemental volume. This overall rate depends on two individual rate coefficients, viz. the rate coefficient for surface reaction and the rate coefficient for gas phase mass transfer. The values of these individual rate coefficients have been calculated from published kinetic data, and these have been plotted in suitable graphs against the relevant variables for rapid calculation of the overall rate of reaction under different conditions. Finally the design procedure for calculation of the total volume of a catalyst bed utilizing the above graphs has been suggested. This procedure simplifies the design of a shift reactor and saves much time.

## Design Equations for Shift Reactor

Since the shift reaction, viz.  $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$ , is exothermic in nature with a heat of reaction of 8970 cal/g. mol. at the average reaction temperature of  $460^\circ\text{C}$ , and the mean molar specific heat of normal synthesis gas-steam mixture undergoing shift reaction is 8.58 cal/g.mol/ $^\circ\text{C}$ , the design material and heat balance equations may be expressed as

$$dV_r = 9.60 \times 10^{-4} F dT/r_R (1-\theta) \quad (1)$$

$$\text{and } \frac{-dx_{\text{CO}}}{dT} = 9.60 \times 10^{-4}/(1-\theta) \quad (2)$$

## Overall Rate of Reaction, $r_R$

The reaction mechanism has been assumed to occur

by diffusion of gas molecules through gas phase followed by chemical reaction at the surface. Under steady conditions, therefore, the rate of mass transfer through gas phase must equal the rate of surface reaction, and therefore

$$r_R = r_g = r_s \quad (3)$$

$$\text{also } r_g = K_g a_v \phi P (X_{\text{CO}} - X_{\text{CO}}^i) = R_g (X_{\text{CO}} - X_{\text{CO}}^i) \quad (4)$$

$$\text{and } r_s = k_r a_s n_v (X_{\text{CO}}^i - X_{\text{CO}}^{\text{eq}}) (\text{Eff. A}/\sqrt{P}) \\ = R_s (X_{\text{CO}}^i - X_{\text{CO}}^{\text{eq}}) \quad (5)$$

From equations 3, 4 and 5

$$r_R = \frac{X_{\text{CO}} - X_{\text{CO}}^{\text{eq}}}{\frac{1}{R_g} + \frac{1}{R_s}} \quad (6)$$

Equation (4) is the usual mass transfer rate equation and equation (5) a modified form of surface reaction rate equation proposed by Mars<sup>1</sup>,  $K_s e^{-E/RT}$  term of his equation has been replaced by  $K_r a_s$  and the factor  $\frac{1}{\sqrt{P}}$  has been introduced, as published information<sup>2,3</sup> shows that rate is proportional to  $\sqrt{P}$ .

## Evaluation of $R_s = K_r a_s n_v \text{Eff. A}/\sqrt{P}$

From published data<sup>1</sup> it is found that for a gas containing 0.1 per cent  $\text{H}_2\text{S}$  and molefraction steam,  $X_{\text{H}_2\text{O}} = 0.7$ ,

$$K_s e^{-E/RT} = 6.24 \times 10^{14} e^{-16,150/T} = K_r a_s \quad (7)$$

Bohlbro<sup>3</sup> and Laupichler<sup>4</sup> have shown that reaction rate depends on molefraction of steam and concentration of sulphur in gas. For a gas containing 2000 ppm  $\text{H}_2\text{S}$ , Bohlbro<sup>3</sup> has shown that rate is proportional to  $X_{\text{H}_2\text{O}}^{0.5}$ . Since in most cases mean molefraction of steam in



catalyst beds is approximately 0.5, the values of  $K_r a_s$ , given by Mars<sup>1</sup>, have been multiplied by  $(0.5/0.7)^{0.5} = 0.845$ . Moe<sup>5</sup> has shown that the value of  $a_s$  for iron oxide-chromium oxide shift catalyst after 50 hours of working is  $4 \times 10^5 \text{ cm}^2/\text{cm}^3 \text{ bed}$ . With this value of  $a_s$ ,  $K_r$  is calculated from  $K_r a_s$  and both  $K_r$  and  $K_r a_s$  are tabulated below. These values are applicable for  $X_{\text{H}_2\text{O}}$ , mean = 0.5 and 1000 ppm  $\text{H}_2\text{S}$  in gas.

TABLE 1

	1	2	3	4
T°K	633	663	693	723
$K_r a_s$	4,770	13,200	37,300	98,000
$K_r \times 10^3$	1.19	3.04	9.3	24.5

	5	6	7	8
T°K	753	773	803	833
$K_r a_s$	224,000	447,000	930,000	1,900,000
$K_r \times 10^3$	56	114	232	475

Effectiveness factor, Eff, in equation (5) depends upon

$$\text{Thiele modulus, } m = \bar{L} \sqrt{\frac{2k_r}{r_0 \text{ Diff}}} \quad (6)$$

$$\text{and is given by Eff} = \frac{1}{m} \tanh m \quad (7)^6$$

$$\text{where } \bar{L} = \frac{V_p}{S_x} \cdot \sqrt{2} \quad (8)$$

for a solid cylindrical particle of height=diameter

$$\bar{L} = \frac{D_p}{6} \cdot \sqrt{2} \quad (9)$$

$$\text{Diff} = \frac{1}{\frac{1}{D_{k-\text{co}}} + \frac{1}{D_{\text{co-g}}}} \quad (10)^7$$

$$D_{k-\text{co}} = 9.7 \times 10^3 \cdot r_0 \cdot \sqrt{\frac{T}{M_{\text{co}}}} \quad (11)$$

$D_{\text{co-g}}$ , molecular diffusivity of CO through gas steam mixture in which shift reaction takes place, has been calculated by the method of Hougen and Watson<sup>8</sup>. The calculated values of Diff are shown in Table 2 against temperature and pressure.

TABLE 2—CALCULATED VALUES OF DIFF,  $\text{CM}^2/\text{HR}$

Temp, °K Pressure, atm	633	663	693	753	803	833
1	258	264	270	281	290	296
2.5	225	235	241	250	263	270
5.0	205	212	219	225	240	250
10.0	172	177	184	188	206	216
20.0	129	133	139	154	161	168
30.0	103	107	113	126	131	138

### Sintering Factor

The sintering factor, 'A', depends on temperature and age of catalyst bed. The design values of 'A' at the average temperature of a particular catalyst bed has been taken as the mean of the values of 'A' after a few months and after a few years.<sup>1</sup> The design values of 'A' have been shown against temperature in Fig. 1. The values of  $R_s$  have been calculated based on  $X_{\text{H}_2\text{O}}$ , mean=0.5 sulphur content=1000 ppm and 'A'=0.5, and these have been shown against temperature, pressure and catalyst particle size (Figs. 2 & 3). It should be remembered that  $R_s$  is proportional to 'A'.  $X_{\text{H}_2\text{O}}^{0.5}$ , mean and is double for sulphur free gas<sup>1,3</sup>. Hence, the values of  $R_s$  (Figs. 2 & 3) are to be multiplied by  $\left(\frac{X_{\text{H}_2\text{O, mean}}}{0.5}\right)^{0.5} \cdot \left(\frac{A}{0.5}\right)$  (factor for sulphur). The factor for sulphur may be assumed equal to 1 for sulphur bearing gases (50-2000 ppm S) and 2 for sulphur free gas (less than 10 ppm S).<sup>1,3</sup>

### Evaluation of $R_g = K_g a_v \phi P$

Mass transfer coefficients for flow of gas through

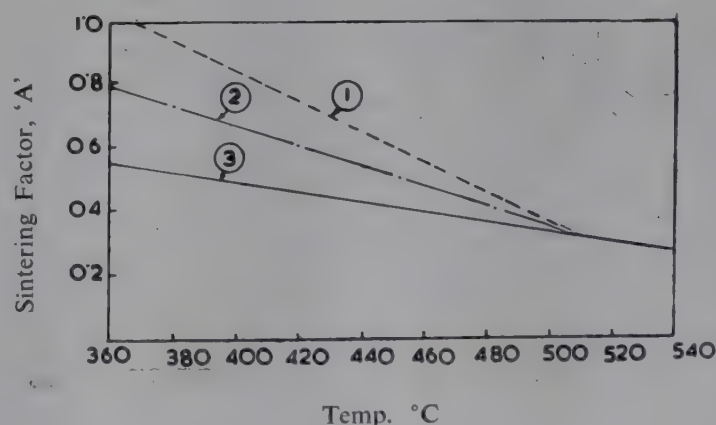


Fig. 1—Dependence of Sintering Factor on Temperature and Age of Catalyst Bed

1. Values of 'A' after a Few Months
2. Design Values of 'A'
3. Values of 'A' after a Few Years



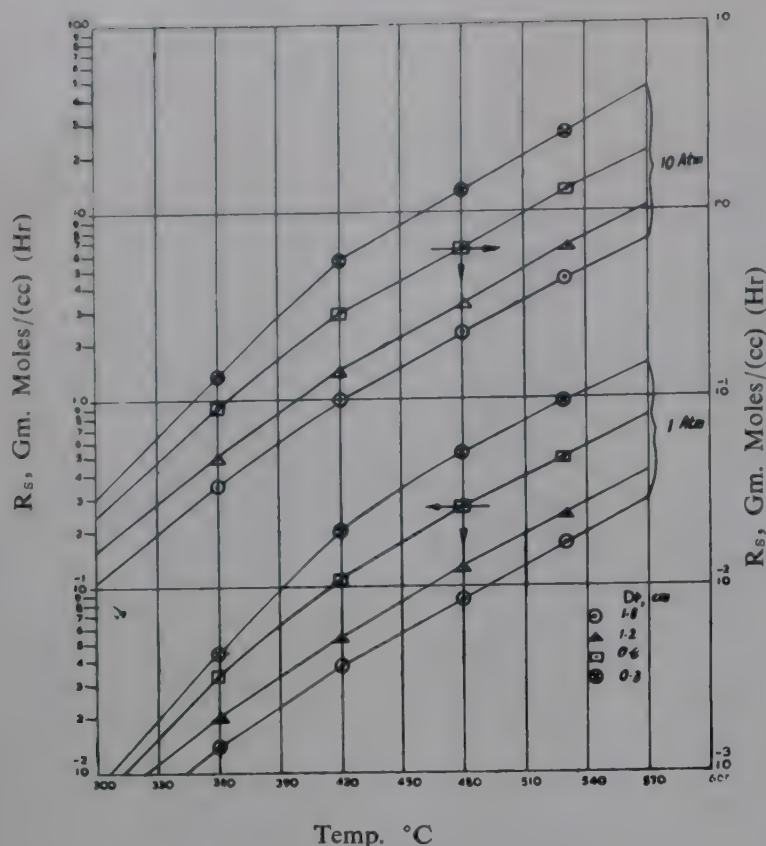


Fig. 2—Values of  $R_s$  at 1 and 10 Atm

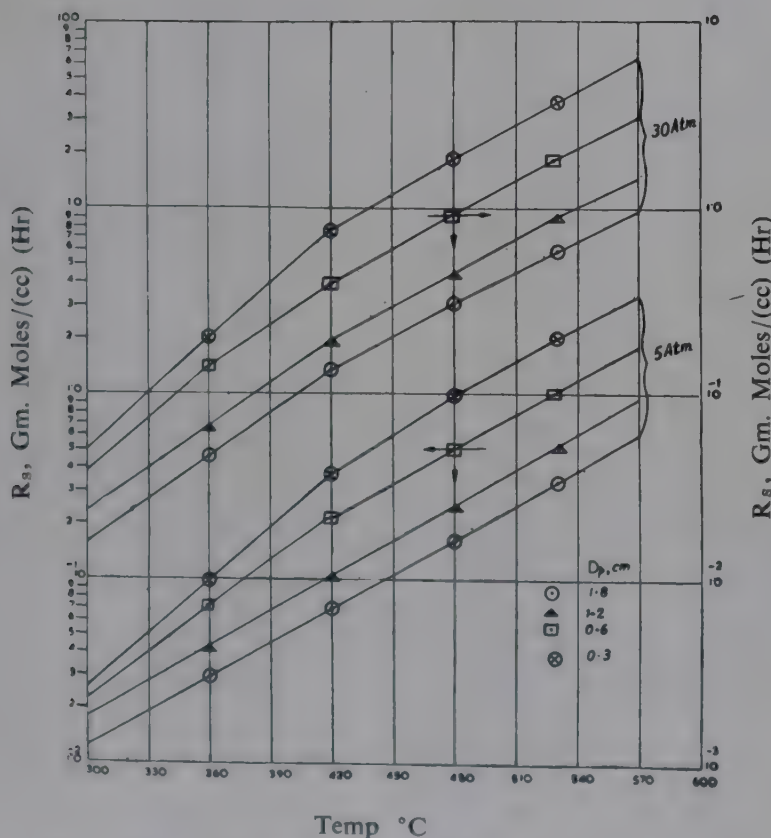


Fig. 3—Values of  $R_s$  at 5 and 30 Atm.

$R_s$  should be corrected by multiplying with  $[(X_{H_2O} \text{ mean}/0.5)^{1/2} (A/0.5)]$  (Factor for S)

Factor for S is 1 for S containing Gas (50-2000 ppm) and 2 for S free Gas (less than 10 ppm).

packed beds of solids have been correlated by Yoshida<sup>9</sup> etc. and Yen and Thodos<sup>10</sup>. Combining these two correlations it is found that

(1) for  $\frac{D_p G}{\mu} = 100-5000$

$$J_D = \frac{K_g P_{gf} M_m}{G} \left( \frac{\mu}{\rho D_v} \right)^{2/3} = 0.60 \left( \frac{D_p G}{\mu} \right)^{-0.41} \quad (12)$$

(2) for  $\frac{D_p G}{\mu} = 0.1-100$

$$J_D = 1.37 \left( \frac{D_p G}{\mu} \right)^{-0.51} \quad (13)$$

According to the method of Hougen & Watson,<sup>8</sup>  $P_{gf}$  for steam-gas mixture in which shift reaction takes place is equal to total pressure and  $D_v$  for diffusion of CO through normal gas-steam mixture  $= D_{CO-g} = 5025 \text{ cm}^2/\text{hr}$  at  $360^\circ\text{C}$  and 1 atm pressure. At other temperatures and pressures  $D_{CO-g} \propto T^{3/2}/P$ . For normal feed mixture  $M_m = 17.0$ ,  $\mu = 0.802 \text{ g./hr/cm.}$  at  $360^\circ\text{C}$  and  $\mu \propto T^{3/4}$  approximately. These physical properties have been found almost independent of change in gas composition during its passage through the shift reactor catalyst bed.

External surface of Catalyst: The factor  $a_v$  in equation 4, is equal to  $6(1-\epsilon)/D_p$  and  $\epsilon$  is usually  $= 0.5$ .

Shape Factor:  $\phi = 0.9$  for solid cylindrical particles of height equal to diameter<sup>9</sup>

In Fig. 4 the calculated values of  $R_g = K_g a_v \phi P$  have been plotted against gas mass velocity,  $G$ , with catalyst particle size as parameter. Effects of pressure and temperature on  $K_g a_v \phi P$  is negligible.

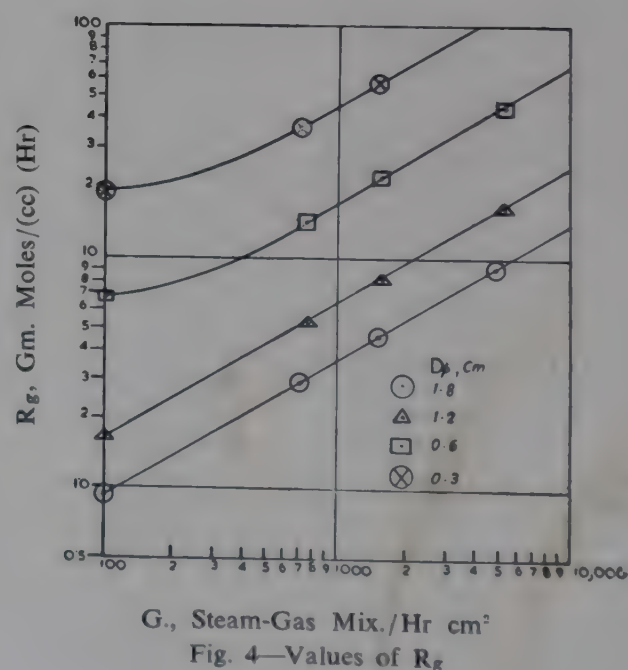


Fig. 4—Values of  $R_g$

## Evaluation of $x_{co}-x_{co}^{eq}$

$x_{co}$  at the inlet temperature is known from feed gas steam mixture composition. Values of  $x_{co}$  at increasing temperatures along a catalyst bed is known by equation (2)

$$-\frac{dx_{co}}{dT} = 9.60 \times 10^{-4} / (1 - \theta)$$

$x_{co}^{eq}$  can be calculated at different temperatures from equilibrium constant  $K_p$  for shift reaction as given by Perry<sup>11</sup>. Calculated values of  $K_p$  are tabulated below

TABLE 3—CALCULATED VALUES OF  $K_p$  AT DIFFERENT TEMPERATURES

T°K	593	633	663	693	723	753	783	813	833
$K_p$	31.4	18.7	13.7	10.0	7.5	5.82	4.50	3.82	3.20

## Design Procedure

An elemental volume of a catalyst bed for shift reaction  $\Delta V_r$  for a given small increase in gas temperature due to heat of reaction is given by equation (1) as  $\Delta V_r = F \cdot 9.60 \times 10^{-4} \Delta T / r_R (1 - \theta)$ . Normally heat lost by radiation and connection is negligible i.e.  $\theta = 0$  and then  $\Delta V_r = F \cdot 9.60 \times 10^{-4} \Delta T / r_R$  (14)

The total volume  $V_r$  of a catalyst bed is obtained by summation of values of  $\Delta V_r$ . The following procedure is suggested.

(a) Process conditions like mean pressure in the bed, inlet temperature, moles of gas in feed and its composition, moles of steam in feed, mass velocity of gas steam mixture are fixed & catalyst size chosen.

(b)  $R_g$  is then calculated from Fig. 4 for the particular values of  $G$  and  $D_p$  chosen.

(c)  $X_{co}$  at inlet condition is calculated from given inlet condition and is then plotted against temperature in an arithmetic graph. The values of  $x_{co}$  at other temperatures in the bed are known by drawing a straight line of slope  $= -9.60 \times 10^{-4} / (1 - \theta)$  as per eqn (2). In the same graph  $x_{co}^{eq}$  calculated from equilibrium constant data and feed composition is plotted against temperature.

(d) From the plots of  $x_{co}$  and  $x_{co}^{eq}$  against temperature, the outlet temperature of the bed is so chosen as to have appreciable difference of  $x_{co}$  from  $x_{co}^{eq}$  at the outlet. As a first trial the choice of outlet  $x_{co}$  may be made at a condition where  $x_{co}^{eq}$  is 75 per cent of  $x_o$  at outlet.

(e) The total temperature rise in the catalyst bed chosen as per (d) is subdivided into a large number of

equal steps. As a rough guide these steps may be taken as 10°C in the primary converter and 5°C in the secondary converter.

(f)  $X_{H_2O}$ , mean in the catalyst bed, presence or absence of sulphur in gas and the value of 'A' at the average temperature of the catalyst bed (from Fig. 1) are noted.

(g) For each step  $R_s$  is noted at the average temperature from Figs. 2 & 3, and this value is multiplied by  $\left(\frac{X_{H_2O, \text{ mean}}}{0.5}\right)^{0.5} \left(\frac{A}{0.5}\right) \times (\text{factor for S})$ . The factor for sulphur is 1 for sulphur bearing gases and 2 for sulphur free gases.  $x_{co}-x_{co}^{eq}$  is also noted at the average temperature of the step from the plots of  $x_{co}$  &  $x_{co}^{eq}$  vs temperature.

(h) Knowing  $R_g$ ,  $R_s$  and  $x_{co}-x_{co}^{eq}$ ,  $r_R$  is calculated by equation (6) and then  $V_r$  is calculated from the design equation  $\Delta V_r = F \cdot 9.60 \times 10^{-4} \Delta T / r_R (1 - \theta)$ .

(i) In this way the elemental catalyst bed volumes for all the successive steps are calculated and their sum total gives the total volume of the catalyst bed.

(j) The same procedure is applied for all the stages.

(k) By further similar trials with different outlet temperatures and outlet  $x'_{co}$ s from a particular bed the optimum condition is found out.

## Discussion

This design procedure has been applied to some of the existing CO-conversion units under F.C.I. Ltd., and a fair agreement of the calculated volumes of beds with actual existing ones has been observed.

## Nomenclature

- A = Sintering factor
- $a_s$  = pore surface,  $\text{cm}^2/\text{cm}^3$  bed volume.
- $a_v$  = external surface of catalyst,  $\text{cm}^2/(\text{cm}^3 \text{ bed volume})$
- $D_{co-g}$  = molecular diffusivity of CO through gas-steam mixture in which shift reaction takes place,  $\text{cm}^2/\text{hr}$
- Diff = mean diffusivity through pores,  $\text{cm}^2/\text{hr}$
- $D_{k-co}$  = knudsen diffusivity for CO,  $\text{cm}^2/\text{hr}$
- $D_p$  = catalyst particle diameter, cm
- $D_v$  = molecular diffusivity of a component through gas mixture,  $\text{cm}^2/\text{hr}$
- Eff = effectiveness factor
- F = total moles of gas steam mixture flowing per hour, independent of extent of shift reaction.
- G = mass velocity of Gas steam mixture,  $\frac{\text{gms}}{(\text{hr}) (\text{cm}^2)}$



$K_g$  = mass transfer coefficient  $\frac{\text{gm moles}}{(\text{hr}) (\text{cm}^2) (\text{atm})}$   
 $K_r$  = surface reaction velocity constant, cm/hr  
 $\bar{L}$  = pore length, cm  
 $m$  = Thiele modulus  
 $M_{\text{CO}}$  = mol. wt. of CO.  
 $n_v$  = molal density, gm moles/(cm<sup>3</sup> gas volume)  
 $P$  = total pressure, atm  
 $p_{\text{gt}}$  = partial pressure of nondiffusing component, atm.  
 $r_g$  = gas phase mass transfer rate,  $\frac{\text{gm moles CO}}{(\text{hr})(\text{cm}^3 \text{ bed volume})}$   
 $r_s$  = surface reaction rate,  $\frac{\text{gm moles CO}}{(\text{hr}) (\text{cm}^3 \text{ bed volume})}$   
 $r_o$  = pore radius, cm.  
 $R_g$  = gas phase mass transfer coefficient =  $k_g a_v \phi P$ , gm moles/(hr) (cm<sup>3</sup> bed volume)  
 $R_s$  = surface reaction rate coefficient  
 =  $K_r a_s n_v \cdot \text{Eff.A.}/\sqrt{P}$ , gm moles/(hr) (cm<sup>3</sup> bed volume)  
 $S_x$  = external surface of a catalyst particle, cm<sup>2</sup>  
 $T$  = temperature °K,  
 $V_p$  = volume of a catalyst particle, cm<sup>3</sup>  
 $V_r$  = catalyst bed volume, cm<sup>3</sup>  
 $X_{\text{H}_2\text{O}}$  = mole fraction of steam in gas-steam mixture  
 $x_{\text{CO}}$  = mole fraction of CO in gas steam mixture  
 $X_{\text{CO}}^i$  = mole fraction of CO at catalyst-gas interface  
 $x_{\text{CO}}^{\text{eq}}$  = molefraction of CO at equilibrium

$\theta$  = fraction of heat of reaction lost by radiation and convection  
 $\phi$  = shape factor  
 $\mu$  = viscosity of gas-steam mixture, gms/(hr) (cm)  
 $\rho$  = density of gas-steam mixture, gms/cm<sup>3</sup>  
 $\epsilon$  = void fraction, usually 0.5 for catalyst packed beds.

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# Load Cell and Its Applications in Engineering

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The advent of load cells has provided an alternative means of automatic industrial weighing and made possible the direct and accurate determination of stresses in certain fields of engineering which could not be made by the conventional means. The basic operating principles of the different forms of load cells, their popular applications, specific advantages and limitations have been discussed.

## Conventional Systems

Till the advent of load cells, the various systems of industrial weighing were based mainly on the principles of lever and spring action. The first step in the conventional system was to reduce a large force, developed as a result of the load to be weighed, to a value where it can be counter-balanced by a much smaller force, by employing innumerable levers. Consequently, the various forms of friction, usually encountered at several points, are harmful to proper scale operation since their characteristics might deviate from what had been envisaged in the design. Much work has been done during the past many years to perfect such systems and make them adaptable to the various and varying demands of the industry, such as (1) providing automatic and continuous recording; (2) enabling remote transmission of the indications and centralized automatic control; (3) providing automatic batching of different materials as per pre-determined quantities; (4) making the system shock-proof and vibration-proof; (5) adapting the system to measure shock load; (6) adapting the system to corrosive and dusty environment; (7) minimizing the frequent checks and adjustments required due to the large number of moving parts and friction points involved, and (8) minimizing the floor space required.

The load cell promises to eliminate most of the above difficulties and provide a reliable and much cheaper device for industrial weighing.

## Load Cell and Its Principle

The basic principle of a load cell consists in subjecting a compact and small unit, known as load element

or cell, directly to the full or a considerable fraction of the stress caused by the load, and measuring the proportional signal transmitted by the element by an indicator or recorder located at a convenient place. The signal is either in the form of a proportional increase in pressure of the liquid trapped inside the load element in the case of a hydraulic load element, or an increase in the electrical resistance of one or more conductors or a semi-conductor located in the load element and subjected to stress in the case of an electrical load element, or an increase in air pressure necessary to counteract the stress caused by the load on the bearing surface of the element in the case of the pneumatic load element. It will be clear that these are remarkable deviations from the conventional systems.

*Electrical Load Cell or Strain Gauge:* The basic principle in one of the popular types is the transference of the load to be measured to a set of four resistance wires (metallic) already in tension, so that two of these wires are elongated by the new stress, while the other two are shortened. The four wires form the four arms of a Wheatstone Bridge and are so connected that the elongated and shortened wires form the opposite arms of the bridge. Due to variation in length, the electrical resistance of the wires also changes, and a measurement of this change of resistance will be a measure of the load applied. The variation in the resistance of the load element due to change of temperature will have little effect on the final reading since the four identical resistance wires are so connected that the thermal changes in two of them neutralize the same in the other two. The secondary instrument connected to the load element can be an electronic recorder and calibrated in terms of load. The strain



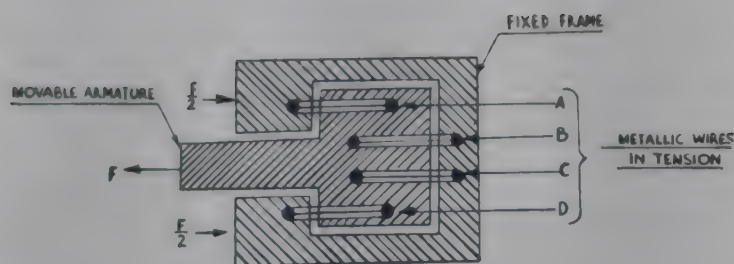


Fig. 1—Unbonded Strain Gauge

gauges are broadly classified into the bonded and the unbonded gauges.

In the unbonded gauges, the fixed frame and the movable armature are held together by a set of four metallic wires under initial tension (Fig. 1). When a tensile load is applied to the armature, wires B and C stretch while A and D are shortened. The reverse is the case when the armature is subjected to compression.

In the bonded type, each of the resistance wires is set in a cloth or paper strip and bonded to a member by a special cement (Fig. 2). When the member is subjected to the load to be measured, it gets elongated or shortened depending on the nature of stress, and the resistance wires cemented on to its surface also undergo the same change in length. The member is generally of a ring shape—being called the stress ring—and the four wires are mounted as indicated so that when two of them undergo elongation, the other two get shortened, thereby providing compensation for ambient temperature variations.

In cases where stresses act in different directions, their directions and magnitudes are determined by arranging three resistance wires in the star or delta

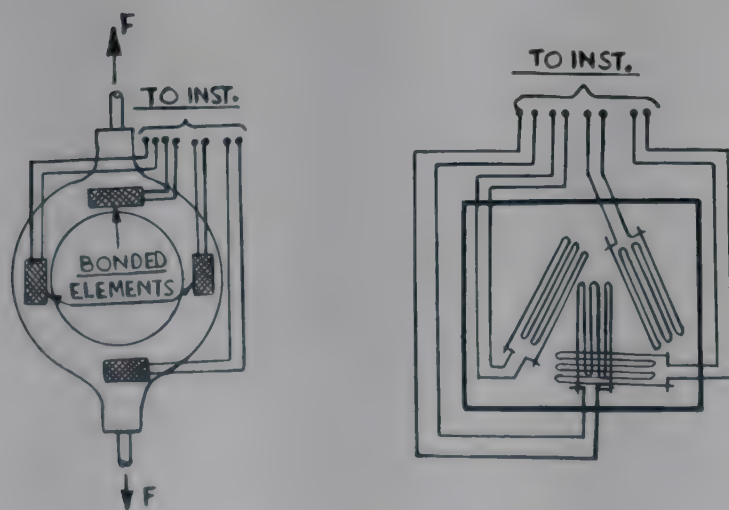


Fig. 2—Bonded Strain Gauge Elements

fashion and measuring the stress carried by each of them. This arrangement, when bonded to the outside surface of pressure vessels, can be used to determine the stress to which the vessel walls are subjected. The bonded strain gauges are also of use in determining vibrational stresses and forces due to impact or acceleration.

The load element may be of a single wire only, in which case compensation for ambient temperature variation can be accomplished by using an additional low resistance platinum wire, which is integral with the load element. It acts as a temperature sensing device and is so chosen that the percentage change in its resistance with temperature variation nearly cancels the percentage change in resistance of the strain sensing element due to ambient temperature variations within a particular range.

A more recent development is to employ a semi-conductor in place of the metallic wire, and such a device is, therefore, known as semi-conductor or solid state strain gauge. It is based on the property of a semi-conductor crystal to undergo a sharp change in its resistance when subjected to tension or compression. It consists of a thin flexible rectangular filament of a single-crystal silicon (the filament size is 0.002" in width  $\times$  0.0005" in thickness  $\times$  5/8 in length) bonded to a suitable base (glass cloth) with integral printed circuit terminals. The strain gauge is so flexible that it can be installed around diameters of 1" or less without fear of fracture of the filament.

Recent advancements in the development of the electrical elements of the bonded type—especially semi-conductor—have extended their application to the field of vibration.

**Hydraulic Load Cell:** In principle, it consists of a metallic welded chamber of small volume connected to a secondary indicating or recording instrument by means of armoured capillary tubing. Both the chamber and the capillary tube are filled with a suitable liquid, generally mercury. The load is transferred to the top surface of the metallic chamber which deflects a small amount and transfers a proportional thrust to the liquid enclosed in the chamber causing an increase in its pressure proportional to the load applied. The other end of the capillary is connected to a suitable secondary instrument, generally a Bourdon tube, also filled with mercury. The increase of pressure in the load cell is thus communicated to the Bourdon tube, causing it to deflect in proportion to the load applied on the cell. The deflection of the Bourdon tube is taken up by suitable kinematic chain so as to move the pointer



of the secondary instrument. Suitable recording arrangement can also be provided.

The welded metallic chamber (load cell) can be of different designs to suit the individual requirements. In one design, called the diaphragm type, it consists of two hard metal diaphragms welded together so that there is an enclosed space in-between for the mercury.

In another design, known as the spool type, the load cell consists of a cylindrical steel body with collars at both ends. A free-to-move invar cylinder located in the mercury chamber provides adequate compensation for variations in ambient temperature.

A third design, known as the ring type, is similar to the diaphragm type except that it has a central hole through which a shaft or loading screw, the stress on which is to be determined, can pass (Fig. 3).

**Pneumatic Load Cell:** Its principle lies in measuring the pressure of compressed air necessary to counteract the downward stress caused by a load on a platform, the pressure being an indication of the load applied (Fig. 4). The application of load on the platform (5) causes the valve rod (6) to move downwards deflecting the diaphragm (7). The tapered end of the valve (3) opens the pneumatic air supply (1) to the diaphragm chamber (8) from where it reaches the support chamber (9) below the loading platform through the orifice (4). When the build-up of air pressure is adequate, the loading platform (5) is lifted up to its original position. This causes the valve rod and its tapered end to rise to their original positions, thereby closing further entry of air into the system. The pressure of air in the diaphragm chamber, which is a measure of the load on the platform, is conveyed to a secondary instrument through suitable piping (2). The secondary instrument is calibrated in terms of equivalent loads.

In another type of the pneumatic load cell, the load changes the position of a flapper through a suitably designed kinematic chain and causes a proportionate pneumatic signal to be conveyed to the indicating or

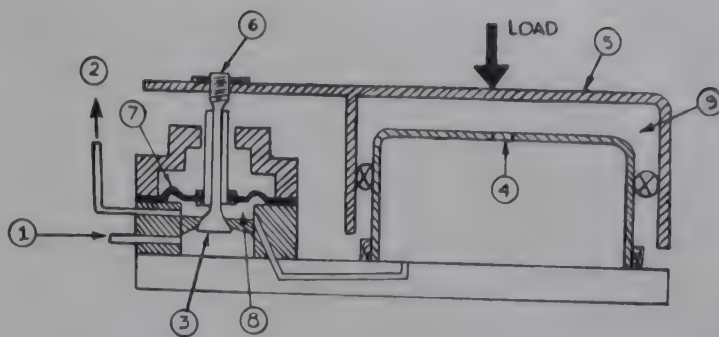


Fig. 4—Pneumatic Load Cell

recording instrument which is calibrated in terms of load.

### Applications

(i) An important application of load cell is in the automatic and continuous weighing of the contents of a storage tank especially in the chemical industry. This is done by having the tank supported solely by a selected number of load cells located on the foundation so that the entire weight of the tank with contents is carried by all the load cells together. It is advisable to employ three load cells since a lesser number may result in lack of stability, while a higher number may cause difficulties due to probable absence of contact between some of the load cells and the tank. The incoming and outgoing lines to the tank are made flexible so as to cause little effect on the load measurements. Either the load cells are connected to equal number of secondary instruments, in which case the sum of the individual readings gives the total weight of the tank and contents, or more economically, the impulses from all of them are added up and fed to a single secondary instrument. The latter arrangement is easily accomplished in the case of electrical load cells, while the former is recommended for the hydraulic and pneumatic cells which require complex devices for the proper summing up of the hydraulic and pneumatic impulses. The secondary instruments of a number of such tanks can be located at any desired point viz. a central control room or a production despatcher's panel, and by having suitable automatic systems, it is quite easy to control the weight of the contents of the tanks by the automatic or remote operation of the inlet and outlet control valves.

It is also possible to reduce the number of load cells required by replacing a few out of them by pivot supports. In such a case, the actual percentage sharing of the total load by the load cells on the one hand and the pivots on the other is to be mathematically ascertained and the readings of the instrument multiplied

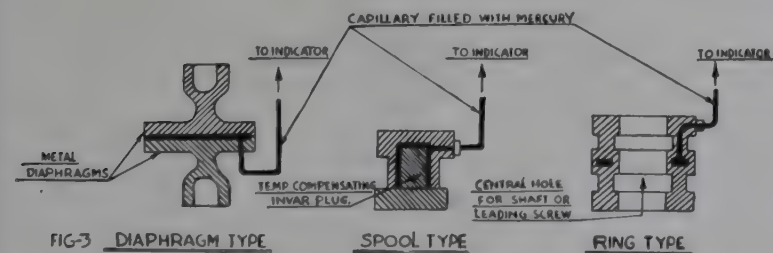


Fig. 3—Hydraulic Load Cell



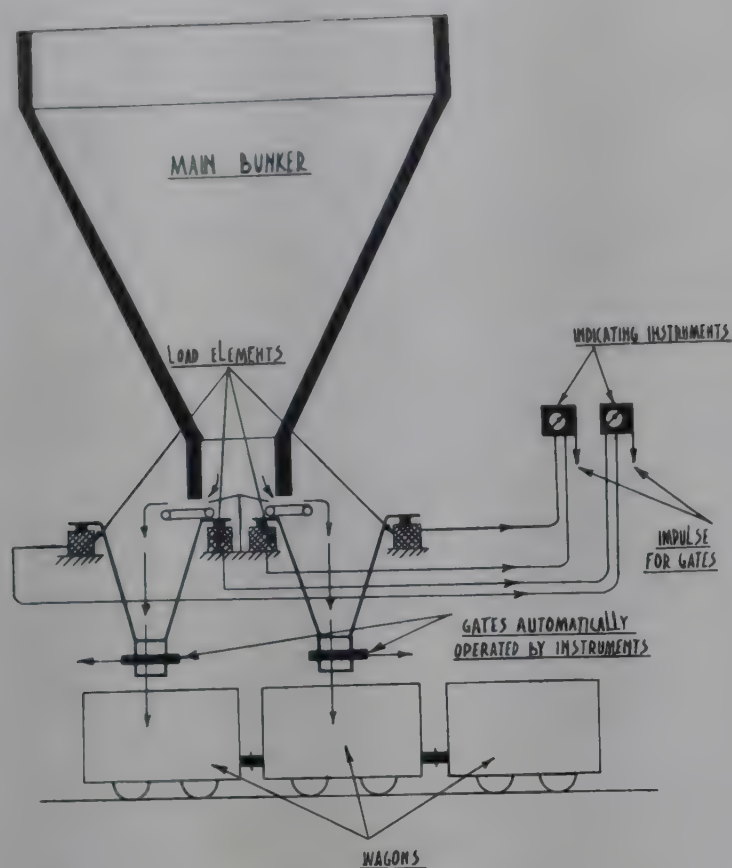


Fig. 5—Load Cell System for loading wagons accurately from a very large Bunker

by a suitable factor to determine the total weight. Alternatively, the scale can be made direct-reading by introducing the necessary amplification factor. It is, however, to be noted that the accuracy of this method is doubtful since it depends on the installation being done precisely according to the design, the pivots being frictionless and also the tank cross sections being uniform throughout.

(ii) Another important application of the load cell is in determining the weight of raw materials and semi-finished and finished products at various stages of manufacture in heavy industries. In the case of raw materials, suitable proportioning and blending are also required besides weight determination.

As for example, in the iron and steel industry, limestone and coke can be weighed and automatically recorded by mounting the load cells in a section of the rail-track and allowing the wagon to pass over that section both when loaded with raw material and when returning back empty. Before charging the blast furnace these raw materials from the storage yard can be automatically weighed and proportioned by centralized automatic control instruments connected with suitably installed load cells. Since the cells are hermetically

sealed and the secondary instruments are mounted in a distant control room, the usual problem of protecting the equipment from the dust-laden atmosphere of the charging station does not arise.

Similarly, in the steel melting shop, the weights of molten pig iron and other raw materials charged into the furnace and of the molten steel can be automatically conveyed to a distant cabin. An interesting application is found in the automatic control of the pouring of molten steel into the ingot moulds. Load cells are mounted on the spreader beam of the hot metal ladle, and the secondary instrument connected to the cells measures continuously the weight of the molten product in the ladle. When the predetermined weight of metal has been poured into the ingot mould—this being preset in the instrument and indicated by the loss of weight of the ladle and its contents—the control equipment coupled to the instrument automatically closes the bottom opening in the ladle by a suitable stopper, thereby shutting off further pouring into the mould.

The weighing of the hot metal, effected at definite points in a rolling mill, goes a long way to have a rigid control on the operational efficiency. Such accurate weighing of ingots, cropped ingot ends and the finished products will give valuable data regarding the actual loss of metal stage-wise during various operations based on which the inefficiency in the process can be localized to one or a limited number of sections.

The thrust on a motor bearing, the load on a crane, the shock thrust at the bearing of a flying shear for slicing of rolling metal, the force between the rolls, the impact exerted by pneumatic forge-hammers, and the axial load on rotating shafts can all be measured continuously and recorded, if so desired, by employing load cells of suitable design. Many of these measurements could not be made directly by the conventional weighing methods. In all the above cases, it is quite easy to couple suitable alarms and tripping devices to the load indicators to protect the equipment from overloading. Load cell manufacturers' catalogues give a variety of ways in which these can be mounted to suit the above cases of loading.

(iii) An important application of the load cell lies in the determination of the various stresses in concrete structures, especially dams. These stresses occur due to: (1) temperature variation in the body of the concrete structure; (2) self loading; (3) water pressure on the upstream of the dam; (4) uplift pressure of water at the foundation of the dam.

The load cells employed are of the electrical type

(strain gauges). The various points at which the above types of stresses are likely to be the maximum are selected from the design data and the cells are embedded at those places at the time of concrete pouring. The load cells for the above purposes are provided with suitable gripping arrangements—generally collars at the two ends—so that their bodies will undergo the same change in length as the concrete. The connecting cables, also of special design, are embedded in the concrete and are connected to indicating and recording instruments located at a common observation post. Extreme care must be taken to ensure the proper alignment of the load cells, since the reliability of the measurements obtained will otherwise become questionable.

(iv) The load cells find extensive application in oil field drilling where they are employed to determine and control the load on the rotary drillers during the drilling operation. Generally hydraulic load cell of special shape is utilized for this purpose. The dead end of the wire rope of the drilling rig is connected to the load cell through the drum of an anchor.

(v) The vibrational forces on the shafts of engines, turbines, motors and pumps, and on the vital elements of aircraft and missile, as also the structural vibrations in ships, submarines, automobiles and railway carriages can be measured and recorded continuously and automatically as a guidance to assessing the probability of any structural failure. Load elements have been attached to propeller blade tips of aircrafts for determining the blade stability at sonic speeds. It is mainly by virtue of the compactness of the gauge elements—as small as 1/32 in—that the stresses occurring under such extremely rapid conditions could be measured. Load elements have also enabled the study of the stresses and reactions of machine and field guns, detonation pressures inside gasoline engines, pressures and thrust reactions of solid propellant rockets, water hammer in pipelines and penstocks, etc.

### Limitations

However, there are certain limitations to the application of load cells, some of which might be enumerated here:

(i) In the case of measurement of stationary loads such as liquid tanks and hoppers, the movement of the structural surface relative to the top surface of the load cell due to ambient temperature variations poses a serious problem, since the vessel surface that is resting over the load cell tends to ride past the load cell. The ultimate effect of such a shift can either result in the cell being eccentrically loaded, or in the cell also moving along with the vessel surface.

To a limited extent, the structural movement can be accommodated by having convex bearing surfaces for the load cells. If the structural movement is however expected to be greater, special sliding arrangements have to be provided such as cantilever bridge or saddles.

(ii) Its performance is subject to error due to ambient temperature variations. Generally compensation provided by different methods may be adequate.

(iii) Unless extreme care is taken to ensure the precise mounting of load cell, the measurements made are likely to be erroneous.

(iv) Its accuracy and also the repeatability of its performance are to a great extent dependent on the materials that determine the characteristics of the resistance wire or the semi-conductor or the diaphragm. In the case of the electrical load cell, the accuracy is generally limited to 0.1 per cent of the full range of the instrument since the output versus applied load characteristic is not strictly linear unless special provisions are made to reduce or eliminate the non-linearity.

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# On the Adsorption of $\text{NH}_4^+$ Ion by Clay from Ammonium Nitrate Solution Containing Calcium Nitrate

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The adsorption behaviour of  $(\text{NH}_4)^+$  ion by a bentonite sample has been studied by varying the concentration of ammonium nitrate solution as well as the proportion of calcium nitrate.

In our previous communication<sup>1</sup>, the adsorption behaviour of  $\text{NH}_4^+$  ion by clay from normal solution of ammonium nitrate, containing varying proportion of calcium nitrate, was reported. It was observed that adsorption falls rapidly if the amount of calcium nitrate exceeds a certain limit in the adsorbing solution. In the present investigation, the adsorption behaviour of  $\text{NH}_4^+$  ion by bentonite has been studied by varying both the concentration of ammonium nitrate solution and the proportion of calcium nitrate therein.

Three different concentrations of ammonium nitrate solution, viz. 1.0, 0.5 and 0.1N each with varying content of calcium nitrate, have been used. The bentonite sample consists mainly of montmorillonite, and exchangeable  $\text{Ca}^{++}$  ion present in it was found to be 32.32 m.eq./100 g. The procedure for the determination of  $\text{NH}_4^+$  ion adsorbed by clay was the same as reported previously.<sup>1</sup>

It has been observed that the adsorption of  $\text{NH}_4^+$  ion by bentonite sample is affected by dilution of the adsorbing solution. As for example, the adsorption values of  $\text{NH}_4^+$  ion from 1.0, 0.5 and 0.1N solutions of ammonium nitrate are 74.0, 73.2 and 41.8 m.eq./100 g. of clay respectively (Table 1). It has been further observed that the proportion of calcium nitrate in the adsorbing solution has a distinct effect on the adsorption of  $\text{NH}_4^+$  ion, and the adsorption value remains almost unaffected up to a certain proportion of calcium nitrate in each concentration of adsorbing solution. Beyond this limit, the adsorption of  $\text{NH}_4^+$  ion decreases rapidly in each case (Table 1 & Fig. 1). This limiting proportion of calcium nitrate, however, decreases with dilution of

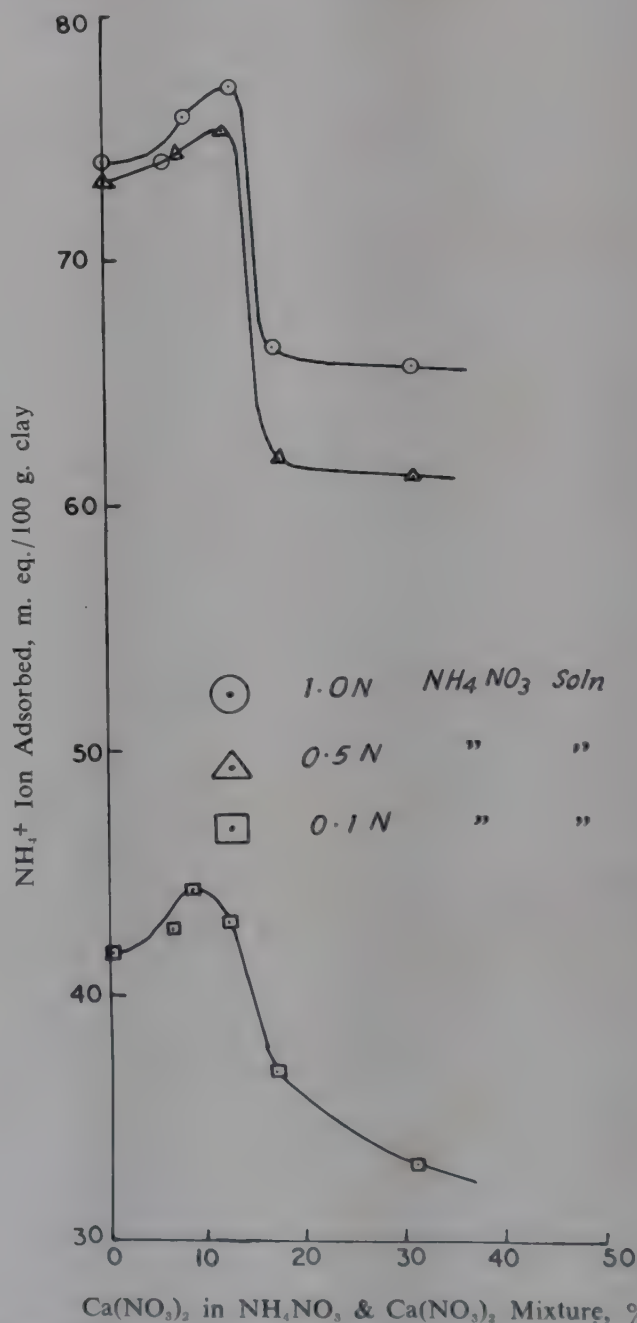


Fig. 1—Effects of  $\text{Ca}(\text{NO}_3)_2$  on  $(\text{NH}_4)^+$  Ion Adsorption by Bentonite

TABLE 1—EFFECT OF  $\text{Ca}(\text{NO}_3)_2$  ON THE  $\text{NH}_4^+$  ION ADSORPTION BY TINPAHARI BENTONITE IN DIFFERENT CONCENTRATIONS OF  $\text{NH}_4\text{NO}_3$

(Exchangeable  $\text{Ca}^{++}$  ion in original bentonite sample = 32.32 m. eq./100 g.)

$\text{Ca}(\text{NO}_3)_2$ in $\text{NH}_4\text{NO}_3$ & $\text{Ca}(\text{NO}_3)_2$ mixture, %	$\text{NH}_4^+$ Ion Adsorbed, m.eq./100 g. Strength of $\text{NH}_4\text{NO}_3$ Soln.		
	1.0N	0.5N	0.1N
0.00	74.0	73.2	41.8
6.35	73.9	—	42.8
8.10	75.7	74.11	44.4
11.94	—	75.1	43.0
13.05	77.0	—	—
16.91	66.4	61.8	37.0
30.60	65.5	61.0	33.3

the adsorbing solution. Thus, in a normal solution, this limiting proportion of calcium nitrate corresponds to 13.05 per cent and those at 0.5 and 0.1N concentration are 11.94 and 8.10 per cent respectively.

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## Glassy Sodium Potassium Phosphates in Prevention of Calcium Carbonate Scale

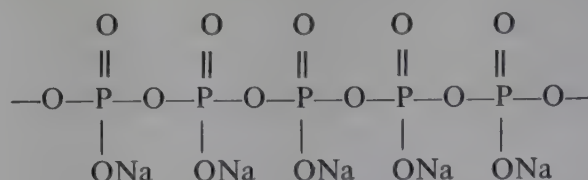
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Glassy sodium potassium metaphosphates containing varying ratios of sodium and potassium show higher sequestering capacity in preventing precipitation of calcium carbonate in water compared to pure glassy sodium metaphosphate. Appreciable sequestering action was noticed for glassy phosphates containing even as low a potassium: sodium ratio as 1:11.

### Introduction

During a comprehensive study by Gupta<sup>1</sup> and Mehrotra and Gupta<sup>2-6</sup> on mixed derivatives of glassy sodium metaphosphate with mono- and di-valent cations, it was observed that the derivatives with potassium show a higher specific conductance as compared with glassy sodium metaphosphate alone or its mixed derivatives with Li, Ca, Ba, Pb, Cu and Zn, the conditions of preparation for the metaphosphates being maintained same in all cases. Glassy sodium metaphosphate is a polyelectrolyte and assumed to have a long chain structure of the type<sup>7,8</sup> given below.



This chain structure probably is responsible for its strong sequestering action in the prevention of calcium carbonate precipitation in water<sup>9,10</sup>. Similar compounds containing potassium in partial replacement of sodium was, therefore, thought to have higher sequestering action on calcium carbonate precipitation in view of



its greater mobility than compounds containing sodium alone.

The present work deals with the preparation of derivatives of the type  $1/n (\text{Na}_x\text{K}_{1-x}\text{PO}_3)_n$  where,  $x=0.917, 0.833, 0.666$  and  $0.500$  and study of their sequestering action on prevention of calcium carbonate precipitation in water.

## Experimental

The glassy phosphates mentioned above were prepared as given in the literature<sup>11,12</sup>. Sodium di-hydrogen phosphate ( $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ , A.R.) and potassium-di-hydrogen phosphate ( $\text{KH}_2\text{PO}_4$ , A.R.) were weighed and mixed according to the stoichiometric ratio in platinum crucible and heated in a muffle furnace at constant temperature ( $800^\circ\text{C}$ ). The molten mass was chilled in water or ice. The details of the heating period and chilling conditions are given in Table 1 for different samples.

TABLE 1

Sample No.	Name	Temp. ( $^\circ\text{C}$ ) & hours	Description
1.	$1/n (\text{NaPO}_3)_n$	800, 1hr	Chilled in ice, observed weight is correct.
2.	$1/n (\text{Na}_{0.917}\text{K}_{0.083}\text{PO}_3)_n$	800, 1hr	Chilled in ice, observed weight is correct.
3.	$1/n (\text{Na}_{0.833}\text{K}_{0.167}\text{PO}_3)_n$	800, 1 hr	Chilled in water, observed weight is 0.3% low.
4.	$1/n (\text{Na}_{0.66}\text{K}_{0.33}\text{PO}_3)_n$	800, 1 hr	Chilled in ice, observed weight is correct.
5.	$1/n (\text{Na}_{0.5}\text{K}_{0.5}\text{PO}_3)_n$	800, 1 hr	Chilled in water, observed weight is correct.

The sequestering effect of 1, 2 and 4 ppm of each sample expressed as  $\text{PO}_4$  was studied over 300 ppm of calcium as calcium carbonate in water. The following procedure was followed for each experiment.

11.2 ml. of stock solution of calcium chloride (equivalent to 300 ppm as calcium carbonate in 100 ml. volume) was taken in a dried glass-stoppered 250 ml. capacity reagent bottle and then distilled water was added so that the total volume after subsequent addition of phosphate solution and sodium carbonate solution becomes 100 ml. Quantities of 0.05, 0.10 and 0.20 ml. of the phosphate solution were added to bottles equivalent to 1, 2 and 4 ppm as  $\text{PO}_4$  respectively in the 100 ml. of total solution. The bottles were shaken for 1 hr. and then 3 ml. of  $0.1\text{M Na}_2\text{CO}_3$  was added and again shaken for 2 hr.

and kept overnight. The solutions were then filtered through dry filter paper in a dry container and analysed for calcium by the usual method of employing EDTA and murexide (Table 2).

TABLE 2—EFFECT OF SAMPLES ON SEQUESTRATION OF CALCIUM EXPRESSED AS  $\text{CaCO}_3$

Sample	Ratio of K: Na	1 ppm	2 ppm	4 ppm
$1/n (\text{NaPO}_3)_n$	—	116.0	179.0	200.0
$1/n (\text{Na}_{0.917}\text{K}_{0.083}\text{PO}_3)_n$	0.0905	137.0	200.0	242.0
$1/n (\text{Na}_{0.833}\text{K}_{0.167}\text{PO}_3)_n$	0.2	137.0	200.0	242.0
$1/n (\text{Na}_{0.66}\text{K}_{0.33}\text{PO}_3)_n$	0.5	148.0	210.0	242.0
$1/n (\text{Na}_{0.5}\text{K}_{0.5}\text{PO}_3)_n$	1.0	157.0	210.0	242.0

It is evident that all derivatives containing potassium show a definite increase in sequestering action of calcium expressed as calcium carbonate compared to glassy sodium metaphosphate (Table 2). The glassy metaphosphate containing the highest proportion of potassium that could be prepared was  $1/n (\text{Na}_{0.5}\text{K}_{0.5}\text{PO}_3)_n$ . It is observed that for 1 ppm of phosphate ( $\text{PO}_4$ ) even in the compound having a potassium: sodium ratio of 0.0905 shows an increase of sequestering capacity from 115 to 136 ppm of calcium carbonate. With increase in the potassium content in the compounds the sequestering capacity increases and at a potassium: sodium ratio of 1, i.e. for  $1/n (\text{Na}_{0.5}\text{K}_{0.5}\text{PO}_3)_n$  the sequestering capacity shows a value of 157 ppm of calcium carbonate.

It was thus thought that instead of using the solid sodium potassium compound of  $1/n (\text{Na}_{0.917}\text{K}_{0.083}\text{PO}_3)_n$  containing the lowest proportion of potassium a mixture of  $1/n (\text{NaPO}_3)_n$  and  $1/n (\text{Na}_{0.5}\text{K}_{0.5}\text{PO}_3)_n$  in solution having the same ratio of sodium-potassium as the former should give similar results, as that of the solid sodium potassium phosphate. Experiments were carried out by mixing two solutions viz.  $1/n (\text{NaPO}_3)_n$  and  $1/n (\text{Na}_{0.5}\text{K}_{0.5}\text{PO}_3)_n$  in a proportion which could correspond in composition with  $1/n (\text{Na}_{0.917}\text{K}_{0.083}\text{PO}_3)_n$ . The rest of the procedure was followed as described earlier and the quantities employed were also same. The values obtained are in good agreement with that of solid derivative of the similar composition (Table 3).

TABLE 3—EFFECT OF SOLID AND SOLUTION ON SEQUESTRATION OF CALCIUM AS  $\text{CaCO}_3$

Sample	1 ppm	2 ppm	4 ppm
$1/n (\text{NaPO}_3)_n$	116.0	179.0	210.0
$1/n (\text{Na}_{0.5}\text{K}_{0.5}\text{PO}_3)_n$	157.0	210.0	242.0
$1/n (\text{Na}_{0.913}\text{K}_{0.087}\text{PO}_3)_n$	137.0	200.0	242.0
Solution of $1/n (\text{NaPO}_3)_n$ 5 ml.+ $1/n (\text{Na}_{0.5}\text{K}_{0.5}\text{PO}_3)_n$ 1 ml.	137.0	200.0	231.0

## Acknowledgement

The authors' thanks are due to Dr. K. R. Chakravorty, General Manager, for his interest in this work.

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# A Technique for Preparation of Thin Sections of Granular Calcium Ammonium Nitrate for Microscopic Examination

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A technique has been developed for the preparation of thin sections of granular CAN for microscopic examination by a dry process, so that studies on its caking phenomenon could be carried out by following changes in its core and surface textures. It requires encapsulating the granules with a thermosetting polymer, which is finally cut, ground and polished in a specified manner to give sections of desired thickness.

## Introduction

In the course of a study of the physical properties of calcium ammonium nitrate (CAN)—a fertilizer—a method was needed for the microscopic examination of samples with respect to crystal growth, porosity and general structure of the particles. As the studies were directed towards revealing the factors responsible for the caking phenomenon of CAN, it was necessary to be able to observe the surface<sup>1</sup> and core textures independently under the influence of diluents, surface coating agents and double salt formation. The preparation and subsequent examination of the thin transparent sections of samples looked attractive, as it allowed minute observation of the internal structure of the particles and the crystal growth. The techniques for

preparing thin sections of hard brittle, geological specimens, like rocks, minerals etc., for microscopic investigation are now well advanced and documented in technical literature<sup>2,3</sup>.

However, to make thin sections of crystalline granules of CAN, which is soft, porous, water-soluble and at the same time very hygroscopic, requires special consideration. An exposure to ordinary atmosphere results in absorption of moisture and change in the characters to a considerable extent. Further, precaution is also necessary at the time of cutting and grinding the specimen in order to avoid distortion or fracture of the sample as it is very soft. The usual methods for making rock specimens are, therefore, not applicable to CAN for the above reasons.



In this study, a technique has been developed which requires encapsulating and impregnating the granules with a thermosetting polymer so that it could be cut, ground and polished by a complete dry process to give thin sections suitable for microscopic studies under transmitted, polarised light.

### Procedure

1. *Polymer Preparation:* The polymer is prepared by treating 100 cc. of stabilized methyl methacrylate monomer with 20 cc. of 20 per cent (w/v) aqueous caustic soda in a separating funnel in order to remove the hydroquinone, present to the extent of 0.1 per cent in the stabilized medium.<sup>4</sup> The mixture is thoroughly shaken and the brown bottom layer is run out after allowing the material to settle. The process is repeated till colouration ceases. Next, the methyl methacrylate is washed with distilled water several times in the funnel till the washings are free from alkali and then dried over about 10 g. of anhydrous calcium chloride. It is then allowed to settle for several hours in a cool dark place. The destabilized liquid so prepared can be stored in this form for a long time. 5 cc. of such treated monomer is taken in a beaker, mixed with 0.003 g. of benzoyl peroxide and heated slowly to about 90°C for nearly  $\frac{1}{2}$  hr. The heating time is adjusted depending on the time required to form a semi-viscous liquid. It is better to stop at a little less viscous state, because then the liquid will be able to enter freely the small fissures in the sample resulting in a compact form and that would resist cracking during grinding.

The above form of the polymer is then allowed to cool to room temperature and is ready for impregnating the specimen.

2. *Impregnation of Sample:* A freshly prepared CAN granule is taken, which had been kept in a dry air-tight container and is placed inside a standard gelatin capsule, the size of which depends on the size of the granule. The liquid polymer is then poured slowly inside the capsule until the granule is completely submerged. Care is taken at the time of pouring so as to avoid possible air-entrainment, which would provide weak points for rupture during the grinding operation. The capsule is then allowed to polymerise at room temperature. Intermediate disturbances may delay the time of hardening. The setting is allowed to proceed undisturbed by placing the capsules in the apertures of a metallic disc-shaped holder specially fabricated for this purpose. This undisturbed condition is maintained till the polymer gets completely set. As this requires much time, another alternative method is to heat the

capsule in the same undisturbed state at a constant temperature of about 55°C for a few hours. Care is taken not to heat the sample in direct contact with the heating arrangement as rapid fluctuations of temperature would not allow the formation of a glass-like bead. Moreover temperature rise may cause phase changes in the sample.

3. *Preparation of Slide:* When the polymer is completely set, the capsule is put in water for dissolving out the gelatine skin. The polymer bead is then ready for cutting and grinding. One side of the specimen is cut with a hacksaw or nylon blade. It is advisable to use a slow speed saw as both the sample and polymer are not very hard.

As the CAN absorbs moistures very quickly, it is not advisable to keep the cut face exposed to atmosphere for a long time. It is a good practice to perform the cutting and grinding operations in an air-conditioned room. The cut face is ground quickly in successive stages and mounted on the petrographic slide. Preliminary grinding may be done on No. 120 abrasive paper (silicon carbide grit). But as the sample is not very hard it can be straight-way ground on No. 400 abrasive paper. The paper is placed on a flat smooth wooden surface or on a glass plate, and the face of the specimen to be mounted on the slide is moved uniformly in a circular way. Special care is taken to avoid deep scratches or rounding at the edges. The surface of the sample is cleaned by blowing in dry air at frequent intervals. Grinding is finally finished with No. 600 abrasive paper or alundum powder over a smooth glass plate. The use of No. 600 abrasive paper was found to give better results. As no liquid can be used for cleaning the polished surface, precaution is taken to clean it with dry compressed air at every stage. The specimen is then cemented on a glass slide with help of Araldite\*, a fixing reagent. Canada Balsam, used mostly for cementing the specimen in petrographic slides, cannot be used in this case as it requires heating over 100°C. The sample is then left overnight in a dry state for giving sufficient time for hardening. Thereafter, the reverse side, (i.e. the top side of the slide) is ground successively with Nos. 120, 400 and 600 abrasive papers till the slide attains about 0.03 mm. thickness. This thickness is most suitable for studies under the transmitted light, ordinary or polarized. At the time of final grinding, maximum precaution is taken not to overgrind the samples which will blur the details. It is advisable to perform the grinding operations in a

\* a product manufactured by CIBA, India

dry box made of Perspex, mounted in gloves. This would remove the possibility of moisture absorption that may come in from atmosphere or even from human respiration. When it has been finally ground, it is carefully cleaned with dry compressed air and immediately sealed thereafter with a clean dry cover glass placed over it, the edges of which are cemented with Araldite. This would stop moisture penetration in the slide which is then kept pressed overnight to give time for hardening. Finally thicker application of Araldite round the edge of the cover glass makes the slide suitable for storage.

### Discussion

This technique was found very suitable for studies on surface properties in general for the sections could be cut at any level of the granules, from the outer layers where coating agents had the maximum influence, or from the inside bulk. Factors dependent upon moisture absorption or variations in temperature, such as recrystallization or bridging of crystallites, can be followed with convenience. A photomicrograph is reproduced in Fig. 1 obtained from a thin section of CAN granules manufactured at FCI, Nangal, showing crystalline structure.

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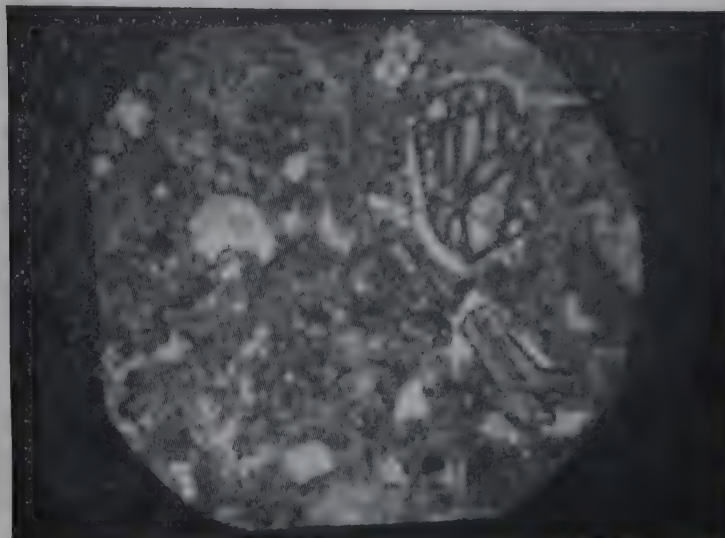


Fig. 1. Photomicrograph of a Thin Section of CAN Granule (Plane Polarized Light  $\times 315$ ).

Dr. B. K. Banerjee, Deputy Superintendent, for his interest in this work.

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# Chromate and Polyphosphate Mixture as A Corrosion Inhibitor in Cooling Tower Waters

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Studies were made on the inhibitive effect of a mixture of chromate (40 ppm. as  $\text{CrO}_3$ ) and polyphosphate (20 or 40 ppm.  $\text{PO}_4$ ) on the corrosion of mild steel, brass and admiralty metal in cooling tower waters in presence of a maximum of 200 ppm. ammoniacal nitrogen, 150 of nitrate nitrogen, 150 of chloride and 200 of sulphate. The inhibitor mixture was found effective in all the cases studied.

In a previous communication<sup>1</sup>, it was pointed out that corrosion of mild steel in a cooling tower water in the Sindri fertilizer factory could be minimized by a dosage of chromate in the range 800-1000 ppm. The cost of maintaining such a residual of chromate is considerable because the material is liable to be reduced to trivalent chromium compound, and also because of its carry-over with the blow-down water. A mixture of chromate and polyphosphate, wherein a much lower concentration of chromate is maintained, has been successfully used<sup>2-5</sup> in cooling waters as a corrosion inhibitor. The present investigation was undertaken to study the effect of this inhibitor mixture under conditions simulating those in Sindri factory. The cooling tower waters in Sindri sometimes contain a considerable amount of nitrate-nitrogen, which is derived from ammonia by bacterial conversion. Hence, the effect of the chromate-polyphosphate combination was studied in presence of increasing amounts of ammoniacal and nitrate-nitrogen, and also in presence of increasing amounts of chloride and sulphate radicals. Corrosion experiments were performed with mild steel, brass and admiralty metal as all these alloys come in contact with the cooling tower waters.

The mild steel specimen analysed as: C0.09, Mn0.46, S0.049, P0.035 and Si0.054 per cent. The brass contained Cu 63.2 and Zn 36.8 per cent; the admiralty metal contained Cu 76.0, Zn 22.8 and Sn 1.2 per cent. The following two types of water were used in the present investigation: (1) Water from the miscellaneous service cooling tower, whose ammoniacal nitrogen content was low; and (2) ammonia synthesis cooling tower water

containing higher amounts of ammoniacal nitrogen. (Table 1).

TABLE 1—CHEMICAL ANALYSES OF COOLING TOWER WATER

*The maximum and minimum values are only presented to indicate the range of their variation*

Sl. No.	Contents and Characteristics	Ammonia Synthesis Cooling Tower Water	Miscellaneous Service Cooling Tower Water
1.	M*		
	(as $\text{CaCO}_3$ , ppm.)	1.8— 10.9	0.6— 0.8
2.	Ammoniacal N, ppm.	30 —131.6	0.5— 2.1
3.	Nitrite + Nitrate N, ppm.	5.2— 7.6	8.2— 21.6
4.	Cl, ppm.	13.7— 35.6	6.3— 23.3
5.	$\text{SO}_4$ , ppm.	43.2— 74.9	36.6— 56.8
6.	Ca, ppm.	36.9— 71.4	45.8— 55.9
7.	Total Dissolved Solids, ppm.	326.0—425.0	240.0—361.0
8.	Total Suspended Solids, ppm.	31.0—146.0	20.0— 60.0
9.	pH	5.3— 7.6	5.5— 6.8

\*M denotes methyl orange alkalinity. None of the samples analysed contained any phenolphthalein alkalinity.

Extra quantities of ammonium nitrate, sodium chloride and sodium sulphate were added to these waters to increase the amounts of nitrogen, chloride and sulphate as desired. Sodium dichromate and sodium hexameta-phosphate were used to introduce desired amounts of chromate and polyphosphate in the waters. The corrosion experiments were performed under conditions of con-

TABLE 2—EFFECT OF CHROMATE AND POLYPHOSPHATE COMBINATION ON THE CORROSION RATE OF MILD STEEL, BRASS AND ADMIRALTY METAL IN COOLING TOWER WATER

Vol. of Soln. —20 l.; Rate of Circulation 2.61 gals./min.; Temp.  $52^{\circ} \pm 1^{\circ}\text{C}$ ; pH 6.1–7.3

CORROSION RATE IN mg./sq.dm./day

Contents in Water	No Inhibitor						40 ppm. $\text{CrO}_4 + 20$ ppm. $\text{PO}_4$						40 ppm. $\text{CrO}_4 + 40$ ppm. $\text{PO}_4$					
	Original Low Ammoniacal Nitrate N			Containing a Total of 200 ppm. Ammoniacal N and 150 ppm. Nitrate N			Original Low Ammoniacal Nitrate N			Containing a Total of 200 ppm. Ammoniacal and 150 ppm. Nitrate N			Original Low Ammoniacal Nitrate N			Containing a Total of 200 ppm. Ammoniacal N and 150 ppm. Nitrate N		
	Mild Steel	Brass	Admiralty	Mild Steel	Brass	Admiralty	Mild Steel	Brass	Admiralty	Mild Steel	Brass	Admiralty	Mild Steel	Brass	Admiralty	Mild Steel	Brass	Admiralty
1. No Additional Cl or $\text{SO}_4$	—	—	—	331.1	23.6	7.3	—	—	—	—	—	—	—	—	—	—	—	—
2. 50 ppm. Cl	—	—	—	363.9	45.9	14.9	—	—	—	12.4	24.6	10.5	—	—	—	9.6	19.2	9.0
3. 50 ppm. Cl 89.7 ppm. $\text{SO}_4$	102.1	13.5	6.3	—	—	—	11.1	8.1	4.8	—	—	—	4.0	5.1	3.2	—	—	—
4. 100 ppm. Cl	—	—	—	375.7	54.0	26.0	—	—	—	18.9	27.8	11.5	—	—	—	15.7	23.1	11.0
5. 100 ppm. Cl 89.7 ppm. $\text{SO}_4$	113.5	14.2	8.9	—	—	—	15.5	10.3	5.6	—	—	—	7.5	8.8	3.8	—	—	—
6. 150 ppm. Cl	—	—	—	396.9	68.7	34.1	—	—	—	25.0	29.2	14.4	—	—	—	22.0	25.5	13.9
7. 150 ppm. Cl 89.7 ppm. $\text{SO}_4$	125.9	14.6	9.4	—	—	—	24.7	12.8	6.3	—	—	—	16.2	12.3	5.8	—	—	—
8. 50 ppm. Cl 100 ppm. $\text{SO}_4$	—	—	—	426.6	72.4	36.3	—	—	—	28.0	29.8	15.1	—	—	—	23.6	27.2	14.8
9. 100 ppm. Cl 150 ppm. $\text{SO}_4$	343.4	20.5	11.3	438.0	77.7	40.8	27.5	13.7	6.9	35.4	31.4	17.3	22.9	13.2	6.3	32.9	27.9	16.9
10. 150 ppm. Cl 200 ppm. $\text{SO}_4$	435.7	24.8	14.7	460.1	84.8	43.7	36.7	17.4	8.9	38.6	35.8	19.9	25.9	15.2	8.1	37.4	29.6	18.6



tinuous aeration and circulation following the method indicated earlier<sup>1</sup>. The method of surface preparation and cleaning of the specimens was also the same<sup>1</sup>. The pH values of the waters used in different experiments were kept in the range of 6.1 to 7.3 by the addition of sulphuric acid or sodium carbonate where necessary.

The results of corrosion experiments with mild steel, brass and admiralty metal are given in Table 2. In the uninhibited cooling tower (Miscellaneous Service) waters, containing low amounts of ammoniacal (0.5 to 2.1 ppm.) and nitrate (8.2 to 21.6) nitrogen, the average corrosion rate of mild steel is 102.1 mg./sq.dm./day in presence of 50 and 90 ppm. of Cl and (SO<sub>4</sub>) respectively. The corrosion rate of brass, under the same conditions, is much lower, and that of admiralty metal is even lower. The corrosion rate of mild steel increases with further increase in chloride and sulphate contents, and with chloride and sulphate concentrations of 150 and 200 ppm. respectively the rate reaches a value of 435.7 mg./sq.dm./day. The corresponding changes with brass and admiralty are small. In case of brass, the corrosion rate increases from 13.5 to 24.8 mg./sq.dm./day, while the change in the case of admiralty metal is from 6.3 to 14.7 mg./sq.dm./day. Corrosion with mild steel decreases markedly in presence of a mixture of 40 ppm. of chromate (as CrO<sub>4</sub>) and 20 of polyphosphate (as PO<sub>4</sub>). It will be observed that there is not much improvement by increasing the amount of polyphosphate to 40 ppm. The corrosion rates of brass and admiralty, which are already

low, are further reduced in presence of chromate + polyphosphate inhibitor.

In the uninhibited cooling tower (ammonia synthesis) waters, containing larger amounts of ammoniacal (200) and nitrate (150 ppm.) nitrogen (made up to these values by intentional additions), the corrosion rates of mild steel, brass and admiralty are considerably higher than in waters containing lower amounts of nitrogen, but the presence of chromate + polyphosphate inhibitor lowers effectively the corrosion rate in all the cases. No pitting or tuberculation was noticed when this inhibitor mixture was used.

It is, thus, observed that a mixture of chromate and polyphosphate can minimize effectively the corrosion of mild steel in cooling tower waters under conditions similar to those used in these experiments and without producing any adverse effect on brass and admiralty metal used in heat exchangers.

The authors wish to thank Dr. K. R. Chakravorty, General Manager, for his interest in this work.

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# *Technical Digests*

## **Cation-Exchanger from Sulphonated Coals**

Cation-exchangers are known to have been prepared from sulphonated coal and used in the treatment of water. Their application is, however, limited, because of lack of stability at high temperature and high pH conditions.

Studies have been carried out in this Division\* of F.C.I. Ltd., on the improvement of sulphonated coal cation-exchanger by heat treatment after further addition of sulphuric acid. Due to its greater stability even at 100°C and pH up to 12, it can be used in the treatment of hot effluents from hot process water softeners and in various types of alkaline liquors, which otherwise could not be treated with the normal coal-based cation-exchangers available at present. The stability of this improved product at high temperature and pH have

been found to be greater when used in fully or partially hydrogen form.

Its preparation comprises the following steps: concentrated sulphuric acid is added to the sulphonated coal and the mixture is heated at 110-250°C for up to about 24 hours with slow stirring. The mass is then cooled and washed till free from acid.

The improved exchanger can be regenerated by sulphuric or hydrochloric acid or by salts. The regeneration of the same product after exhaustion can be repeated innumerable times without any deterioration of the material.

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\* 'A Process for Preparation of Improved Cation-Exchanger from Sulphonated Coal', Indian Pat. No. 80212 (Inventors: A. C. Nanda, B. K. Dutta & Dr. K. R. Chakravorty).



# Notes & News

## Waste & Effluents in Chemical Industries

With the growth of industrialization of India, the disposal of industrial and trade wastes is becoming a problem. The rivers, which are the chief source of water for industrial and potable use, are getting more and more polluted with toxic industrial wastes and effluents. In recent years there is a growing demand for abatement of pollution of water and other insanitary conditions arising out of improper disposal of effluents from industries, and therefore the Indian Standards Institution has prescribed certain requirements for (i) inland surface water subject to pollution, and (ii) industrial effluents discharged into inland surface waters. Even in the Factories Act, there are statutory provisions for the factories for obtaining prior approval for the disposal of their trade wastes from the public health and municipal authorities and the Inspectorate of Factories.

The Sindri unit of the F.C.I. Ltd., being the first major industrial enterprise of the Indian Government, is very much alive to the effluent disposal problem and therefore organized a seminar on 'Wastes and Effluents in Chemical Industries' during May 2 and 3, 1965, under the presidency of Sri A. N. Singh, Chief Inspector of Factories, Bihar.

In all 29 papers, covering different aspects, were presented, followed by lively discussions in which about sixty outside delegates and members from the Planning and Development Division and Sindri and other units of F.C.I. Ltd., participated. The seminar was divided into the following sections: (A) Characteristics of Chemical Industries Waste and Effluents; (B) Industrial Waste and Effluent Treatment; (C) Industrial Waste and Effluent Treatment Plant; and (D) Miscellaneous Aspects of Industrial Waste and Effluents.

The following papers from the P & D Division were read: (i) 'Algae in Waste Treatment' by G. S. Bhattacharyya, G. S. Roy & B. K. Dutta, (ii) 'Removal of Nitrogen from Fertilizer Factory Effluents by Biochemical Nitrification and Denitrification' by A. C. Das, J. A. Khan and

B. K. Dutta, (iii) 'Study of Effluents of Sindri Fertilizer Factory' by R. R. Prasad and B. K. Dutta, and (iv) 'Recovery of Ammonium Sulphate Going Into Damodar River from Sindri Fertilizer Factory' by A. K. Roy, B. B. Roy and A. Mukherjee. From the other units of F.C.I. Ltd., also, several papers were presented, viz. (i) 'Problems of Standardization of Wastes and Effluents with Special Reference to Trombay Fertilizer Factory' by M. W. Desai and M. S. Varde (Trombay), (ii) 'Nature of Wastes and Effluents from the Sindri Fertilizer Factory' by M. Theyyanni (Sindri), (iii) 'Disposal of Waste in Phosphatic Fertilizer Plant' by S. R. Pandey (Sindri), and (iv) 'Effluent Disposal at Nangal' by R. D. Sharma and M. G. Garg (Nangal).

In their paper† on 'Nitrogen Removal from Fertilizer Factory Effluents by Biochemical Means', A. C. Das, J. A. Khan and B. K. Dutta have worked out a method for nitrogen removal by biochemical nitrification and denitrification. They have developed a cultural complex of nitrifying bacteria with the help of which ammoniacal oxygen up to 2000 ppm. can be oxidized mostly to nitrous and partly to nitric acids by continuous aeration for about 40 hours. After neutralizing the acidic solution to a pH about 7.2-7.8 by magnesium carbonate, it was treated in another vessel containing mixed cultures of anaerobic microorganisms and incubated at room temperature. They have observed that a solution containing about 1500 ppm. of nitrite nitrogen can be denitrified in about 20 hours. In case effluent containing about 1500-2000 ppm of ammoniacal nitrogen is treated by nitrification and denitrification, 60 hours' retention period will be necessary.

Of about 9 million gallons of water consumed daily in the Sindri Fertilizer factory, about 4 millions are discharged in river *Damodar* as a combined effluent, drawn mainly from the following sections: power house and coke oven, gas, ammonia,

sulphate, urea and double salt plants. Since the present flow of the river is drastically reduced during a certain part of the year, the discharge of the effluents upstream of the water pumping station might cause contamination in the water supply. R. R. Prasad and B. K. Dutta have studied the characteristics of the effluents from the different plants and have suggested that the possible contamination of the intake water can be avoided by diverting some of the combined effluents in a manner so that it meets the river downstream of the water supply intake. Accordingly, the effluents from the coke ovens and gas plants have been diverted into the drain carrying effluents from ammonia and sulphate plants and discharged without any treatment into the river downstream. The authors have also given a scheme for the recovery of ammonia from coke oven ammonia liquor which will remove one of the causes of ammonia contamination of the river.

In the Merseburg's process of ammonium sulphate manufacture by the gypsum-ammonium carbonate reaction, followed in the Sindri Fertilizers factory, the chalk sludge is filtered, washed and sent to the Dorr thickener of the adjoining cement factory. The overflow of the thickener, which contains ammonium sulphate, is allowed to flow as waste into the river *Damodar*. This, apart from causing loss of the fertilizers, increases ammonia content of the river water, and by the action of nitrifying bacteria, a substantial amount of nitrate is produced which is reported to be harmful. A. K. Roy, B. B. Roy and A. Mukherjee have formulated a scheme for the recovery of ammonium sulphate from the overflow of the Dorr thickener. The chalk from the secondary filters will be repulped with condensate (and demineralized water) to give a slurry with 31 per cent (by wt) of total solids. This slurry will be pumped to the Dorr thickener in the existing line. The underflow from the thickener will then be taken out as usual for cement production, but the overflow, containing about 2 per cent ammonium sulphate, will be sent back to

† Technol., 2(1965), 1, 10.



the Sulphate plant for reacting with ammonium carbonate solution for precipitating out the dissolved lime as calcium carbonate, which can be removed by filtration. The filtrate can be used in different plants. The authors have given the material balance and cost estimate. This scheme is now being implemented by the authorities of the Sindri Fertilizers factory.

In their paper, G. S. Bhattacharyya, G. S. Roy and B. K. Dutta have given a review on the application of the algal lagoons, commonly known as oxidation ponds, for treatment of domestic and industrial wastes. Such ponds, where waste water is impounded, favour algal growth, and have advantages over the conventional sewage treatment methods due to their lower initial cost where land is cheap. They have minimum operation and maintenance problems when properly loaded. Such types of ponds are used for treatment of organic industrial wastes that are amenable to biological treatment. Algal treatment of industrial wastes emanating from nitrogenous factories, containing much higher concentration of ammoniacal nitrogen than met with in sewage, is theoretically possible.

#### Naphtha-based Town Gas Industry in India

There has been a definite shift towards increasing demands for clean fuels for domestic cooking from steep rise in the consumption of kerosene, LPG and electricity in recent years. Today over 500,000 tonnes of kerosene are consumed mainly in urban areas, for domestic cooking only, causing strain on our foreign exchange position. Gas has been accepted as a modern fuel for domestic, commercial and industrial use because of advantages like its smokeless and ashless burning qualities. Its thermal efficiency is also high—60 per cent, next only to that of electricity (76 per cent). In cheapness it is next to coke—the effective price of coke is 6.2 np/1000 k Cal to 7.90 np of gas. If town gas can be made available at 18-25 np/Nm<sup>3</sup> (Rs. 4.75-6.60/1000 cu/ft), it would be quite an economic and suitable fuel.

In a paper [Science & Culture, 31 (1965), 1, 4-17,] K. K. Bhattacharyya has presented a plan for the development of town gas industry in India based on naphtha obtained from crude petroleum. Large-scale availability of cheap oil fractions and development of convenient processes to make suitable gases are leading to the introduction of oil-based processes. In town gas, the ratio of H to C is more than in oil or coal.

In the gasification processes, the required excess hydrogen is introduced in the form of steam. The more H/C ratio in the raw material, the less is the steam required. With changing over from coal to heavy oil, gas oil, light naphtha, natural or refinery gases—materials having increasing H/C ratio—the heat requirement for gasification becomes less, and consequently higher process thermal efficiencies can be obtained and the amount of by-products decreases and purification becomes simpler, requiring less equipment. The latter lead to a decrease of plant costs and the process

becomes less dependent on by-products credit (Table 1).

In the oil gasification processes developed in recent times, the feed hydrocarbons are cracked or reformed with steam over a catalyst bed or simply thermally. The majority of these processes can use variable feedstocks from light to heavy oils. The selection of any one of these processes at a particular place will primarily depend upon the feedstock, nature of operability, quality of gas required and other local conditions (Table 2).

TABLE 1—APPROXIMATE CAPITAL COSTS OF GAS PRODUCTION IN U.K.

Process	£/therm/day	Rs/10 <sup>6</sup> Kcal/day
Coal Carbonization (Coke Oven)	50-60	26000-31600
Coal Gasification (Lurgi)	33-47	17400-24700
Oil Gasification—partial oxidation and refinery gas enrichment	26-30	13700-15800
Oil Gasification—cyclic (heavy oil)	20-30	10500-15800
Coke & oil gasification—carburetted water gas	15	7900
Oil Gasification—cyclic (light distillate)	12-18	6300-9500
Gas reforming—cyclic	10-13	5250-6850
Oil gasification-pressure steam reforming & LPG enrichment	9-15	4750-7900

TABLE 2—PROCESSES OF TOWN GAS PRODUCTION FROM PETROLEUM FRACTIONS

#### I. THERMAL

##### (a) Cyclic

1. Curbur. water gas
2. Jones New Process
3. Refractory Screen Process
4. Twin Generator Process
5. Hall high BTU Process
6. Semet Solvay Regenerative Reverse flow Process
7. King Process
8. Industriebedarf Process
9. Ibing-ibeg Process
10. Koppers Process

##### (b) Continuous

1. GEIM
2. Gas Light & Coke Co.
3. Dayten-Faber
4. T.P.C.
5. Otte
6. Hercules

##### (c) Partial Oxidation

1. Shell
2. Texaco

#### II. CATALYTIC

##### (a) Cyclic

1. ONIA-GEGI
2. SEGAS
3. UGI-CCR
4. ONIA (Semi-continuous)
5. CCR-Ibeg
6. Micro-Simplex
7. SSC-Cyclic Catalytic (Stazione sperimentale per i combustibile)

##### (b) Reforming of Light Distillates

##### (i) Cyclic

1. Stein et Roubaix
2. Gaz de France P-9 & P-12

##### (ii) Continuous

- A. Autothermal, high density gas
  1. CGCF-distigaz
  2. Grande Paroisse Air Cracking
  3. Koppers-Hasche
- B. Endothermal, high pressure
  1. ICI Process
  2. Chemice process
  3. ONIA-GI



In coming years there will be a surplus of light distillates or naphtha which is estimated at 1.3 and 2.8 million tonnes by 1966 and 1971, and any effort to reduce kerosene consumption by utilizing surplus naphtha will improve oil industry's economy.

Assuming a naphtha price of Rs. 110/- per tonne delivered to works, the production cost of gas would be about 9.04-9.24 np/Nm<sup>3</sup> equivalent to Rs. 2.39-2.43 per 1000 cu.ft. The capital cost of such a plant would be only Rs. 4.5 to 5 million.

The actual price at which naphtha will be supplied to industries in our country has not yet been fixed, but considering the present c.i.f. prices at Indian ports as also its fuel value, the ex-refinery price of naphtha is expected to be Rs. 70-80 per tonne depending upon the location of the refinery. At a naphtha price of Rs. 70/- per tonne, the production cost would be 7.4 np/Nm<sup>3</sup> equivalent to Rs. 1.95 per 1000 cu.ft., and at price of Rs. 150/- per tonne gas production cost would be 11.09 np/Nm<sup>3</sup> equivalent to Rs. 2.92 per 1000 cu.ft.

The ex-works selling price of gas would be a little higher. If the capital cost is to be written off in 5 years, as with modern

petroleum plants, the selling price would be about 20 per cent higher than the production cost. The ex-works price of gas in different places in India (naphtha prices from Rs. 70-150/te) would therefore lie between 8.9-13.3 np/Nm<sup>3</sup> equivalent to Rs. 2.34-3.51/1000 cu.ft. respectively.

Assuming that to distribute gas from a 105,000 Nm<sup>3</sup>/day plant, operated at an average load factor of 0.8, say in cities like Lucknow or Poona, a network of 450 miles length would be required which may cost Rs. 1.5 to 12 lakhs per mile to be amortised in 40 years and that its operation, maintenance and overhead costs will approximate to Rs. 1000/- per day, the author has estimated distribution cost of gas as 6.67-8.53 np/Nm<sup>3</sup>, which is equivalent to Rs. 1.76-2.25/1000 cu.ft. respectively. Adding this distribution cost, the price of town gas at the consumer's end would be between 15.6 and 21.8 np/Nm<sup>3</sup> at any town.

The author has made estimates of the probable demands for gas in 17 towns/cities with population above 4 lakhs, assuming that 20-30 per cent of the people depending upon the location of the town and the normal availability of fuels there might turn to gas cooking (Table 3).

TABLE 3—ESTIMATION OF GAS DEMANDS IN DIFFERENT TOWNS WITH MORE THAN 4 LAKH POPULATION

(All figures in thousand)

Town	Population	Estimated gas consumers	Estimated demand, 10 <sup>3</sup> Nm <sup>3</sup> /day			
			Present			After 5-10 Years
			Domestic	Others	Total	
1. Ahmedabad	1,206.0	362.0	135	70	205	350
2. Agra	508.7	152.7	57	13	70	125
3. Allahabad	431.0	86.2	32	18	50	90
4. Amritsar	398.0	120.0	45	25	70	120
5. Bangalore	1,206.0	240.0	90	50	140	250
6. Hyderabad	1,251.1	267.0	100	50	150	300
7. Jaipur	403.4	101.0	37	23	60	100
8. Kanpur	971.1	291.0	109	91	200	400
9. Lucknow	755.0	165.0	62	38	100	160
10. Madras	1,729.1	519.0	194	186	380	500
11. Madurai	425.0	106.0	40	25	65	100
12. Nagpur	690.3	172.5	65	35	100	200
13. Poona	737.4	187.0	70	40	110	200
14. Varanasi	489.9	122.5	46	14	60	100
15. Bombay (Greater)	4,100.0	1,207.0	500	200	760	1,320
16. Calcutta (Greater)	5,500.0	835.5	300	375	675	1,250
17. Delhi	2,500.0	737.7	300	150	450	665
Total	5,671.4				3,645	6,230

## East German Nitrogen Industry

One of the significant aspects of post-war development in E. Germany has been the emergence of the heavy chemicals industry, which contributed 15.6 per cent of the total of 78,110 million marks gross industrial production. Much of this growth can be attributed to the abundant reserves of brown coal, salt, gypsum and lime. E. Germany has built up a large-scale nitrogenous fertilizer industry, second only to U.S.S.R. among the communist countries.

Ammonium sulphate has continued to dominate, but its output has relatively been constant since 1955. On the other hand, calcium ammonium nitrate has been produced on an increasingly large scale—35.2 per cent of the total fertilizer production in 1963 compared to 26.8 per cent in 1950. Of the other nitrogenous fertilizers, calcium cyanamide and potassium ammonium nitrate are the most important, while urea and complex fertilizers have not as yet made any significant impact.

At present there are only two plants, viz. at Leuna and Piesteritz, producing synthetic ammonia for the manufacture of nitrogenous fertilizers. The Leuna works, formerly one of the key complexes of I. G. Farbenindustrie, has been rebuilt entirely after second World War, and by 1953 it achieved its prewar level of 300,000 tpa N. Since then new facilities have been added and the complex has a current annual capacity of 400,000 tpa N using the Haber-Bosch process using coke oven gas as a feedstock. While a small proportion (60,000 tpa N) is used for technical purposes such as manufacture of caprolactam, the bulk is used for manufacturing nitrogenous fertilizers either on site or by supplying to other units at Wolfen, Bitterfeld and Sondershausen. Most of the ammonia is converted to ammonium sulphate (750,000 tpa) by the gypsum process, while small amounts of ammonium nitrate, ammonium sulphate nitrate and urea are also at Leuna.

At Piesteritz, south of Berlin, about 40,000 tpa of N is produced using Fauser-Montectini process based on electrolytic hydrogen. Now entirely modernized, this plant also produces calcium cyanamide, urea and complex fertilizers based on furnace phosphoric acid. Another 40,000 tpa complete fertilizer plant will be installed in the near future at Piesteritz.

There are 3 smaller plants at Wolfen, Bitterfeld and Sondershausen, having a combined capacity of about 120,000 tpa



of N, producing mainly calcium ammonium nitrate and small quantities of sodium nitrate. Potassium ammonium nitrate is also produced in small quantities at Sonderhausen.

Plans are in hand for a large new fertilizer complex, to be established at Schwedt-on-Oder near the Polish border, near a large refinery and petro-chemical plant using crude oil transported from U.S.S.R. by the Friendship pipeline. The contract, valued at £3.6 million for the design and construction of a 510 tpd ammonia plant, has been awarded to Humphreys & Glasgow Ltd. Ammonia from this plant will be supplied to a nitric acid and ammonium nitrate plant to be built by French Schneider-Creusot group. The ammonia plant will incorporate the latest I.C.I. reformation and ammonia processes.

E. Germany has built up a large-scale export trade in nitrogenous fertilizers, like ammonium sulphate, CAN, etc., exporting mostly to E. European countries, U.A.R., Yugoslavia, Greece and India.

[Nitrogen, No. 32, (1964), 24-26]

#### New French Ammonia Process

Societe Chimique de la Grande Paroisse has developed a process, based on a new catalyst and reported to be well-suited for high pressure reforming (300-1000 psig), which require a very small amount of power without increasing consumption of raw material and fuel. Besides adapted to various types of feedstocks and having excellent reforming efficiency, the catalyst has a marked sulphur resistance. When carbon forms on the catalyst due to excessive sulphur, it can be removed by increasing the steam rate without irreversible damage to the catalyst.

Below are given data for a 400 tpd capacity plant: For an overall consumption of naphtha (both feedstock and fuel) of 0.76 lb. of naphtha per lb. of ammonia, the power requirement from external sources does not exceed 180 kWh per s.ton of ammonia, which is hardly more than the consumption of pumps and auxiliaries such as refrigeration. Further refinements now under study may even bring this down to perhaps 60-80 kWh without increasing the fuel consumption. Moreover, a moderate increase in Btu consumption corresponding to less than 0.05 lb. of naphtha per lb. of ammonia can eliminate completely the external kW requirements.

[Nitrogen, No. 32, (1964), 33]

#### Small Ammonia Plants

Constructors like Girdler Corpr., Foster Wheeler and J. F. Pritchard in U.S.A. have developed packaged 50-60 s.tpd anhydrous ammonia plants to fulfil the requirements of a self-contained agricultural area or a developing country. Two 60 s.tpd plants have already been delivered by Girdler.

The mixture of hydrogen and nitrogen is prepared by passing a gas, such as natural gas, mixed with steam over a catalyst at a high temperature and pressure. The gas is reformed to  $H_2$ ,  $CO$ ,  $CO_2$  and  $CH_4$ . This reaction is carried out in a fixed chamber in which the catalyst is contained in stainless steel vertical tubes. The nitrogen is secured from air by adding air to the gas from the first step, known as primary reforming. The methane content of the gas from the primary reformer is used for burning the oxygen content of the air and supplying the nitrogen in the proper relationship to the hydrogen. This reaction is carried out in a catalyst filled vessel, the secondary reformer. The exit gas from the secondary reformer is then mixed with additional steam over a catalyst where  $CO$  is converted to  $CO_2$  and  $H_2$ . This gas, now composed of  $H_2$ ,  $CO_2$  and small quantities of  $CO$  and  $CH_4$ , is then cooled by heat exchange and water-cooling.

From the gas,  $CO_2$  is removed by reacting with monoethanolamine (MEA) and  $CO$  and the remaining amount of  $CO_2$  by hydrogenation. The compression of the gas is accomplished in a multi-service compressor.

To make a ton of ammonia in the 60 s. tons pd gas-engine driven Ammopac requires 39,720 SCF of 1000 Btu/SCF natural gas at 240 psig, 106 kWh of electricity, 1820 lb. of steam at 240 psig, 4880 lb. of boiler feed-water at 280 psig, and 0.3 lb. of MEA. In addition, 88350 U.S. gallons of cooling water is circulated through the plant. The delivered cost of the plant is estimated at \$ 2.0 million.

[Nitrogen, No. 32, (1964), 27-29]

#### Fertilizer Industry in U.A.R.

Among the main problems facing the current industrialization programme of Egypt are the very high rate of population increase (2.5 per cent/yr) and the shortage of cultivated land (only 3 per cent of the total land area is under cultivation). Agriculture is restricted to the Nile valley and Nile delta with sugarcane, wheat,

maize, rice and cotton as the most important crops. Agricultural expansion is being approached in two ways, by reclaiming desert land involving costly irrigation projects and by intensifying the cultivation of the existing productive area.

More intensive cropping of the land, with 2 or 3 crops a year has prompted the Egyptian Government to place much emphasis on increasing the use of fertilizers. Egyptian soils are relatively rich in potash and their principal need is for nitrogenous and phosphatic fertilizers.

While a substantial proportion of demand for superphosphate is still met by imports from Yugoslavia, Spain and France, production of superphosphate is undertaken by two plants, both situated at Kafr-el-Zayat, north-west of Cairo, which have a total capacity of 200,000 tonnes. Both plants are planning large-scale expansion by this year which will double their capacity. A new plant is planned at Asyut, which will be capable of producing 200,000 tonnes of superphosphate annually. When this project is completed in 1965, Egypt will be in a position to meet the internal demand almost wholly through domestic production.

Nitrogen is the most important plant nutrient used in Egypt indicated by the ratio 2.64: 1 for N and  $P_2O_5$  consumption. Only three types of nitrogenous fertilizers have been produced and that too concentrated on relatively low-analysis products.

Calcium nitrate is produced at the plant of Societe' el Nasr d Engrais et d' Industries Chimiques at Attaka, near Suez, which came on stream in 1950, and now approaching full capacity, 450,000 tpa N, but facilities for the manufacture of ammonium sulphate have recently been completed and current overall capacity is estimated at 70,000 tpa. During the present 5-year plan, a Koppers-Totzek gas plant, a Linde-Fraenkl air liquefaction plant and a shift conversion plant are under installation at Attaka raising capacity to 170,000 tonnes of N. The partial oxidation plant will be able to produce synthesis gas from refinery gas or light naphtha. Under a recent agreement with the Government and two firms viz. B.A.S.F. and Fredrich Uhde, further facilities will be installed making possible the production of an additional 275,000 tpa of calcium nitrate and also 165,000 tpa of CAN.

A second synthetic ammonia plant, that of Egyptian Chemical Industries Co.,



is in operation at Aswan, which was built in 1960 by a consortium of German and French constructors. Its current ammonia capacity is 104,000 tpa N, based on electrolytic hydrogen, which is used to manufacture CAN.

A large coke and chemical works is under construction at Helwan, south of Cairo, and based on its coke oven gas ammonia will be produced for use in manufacture of CAN with Soviet aid. Its nitric acid plant, having a capacity of 170,000 tpa, using Stamicarbon process, will be built by WMF-Stork-Werkspoor group.

A new nitrogen complex was planned to be built near Alexandria.

The demand for fertilizer nitrogen has increased markedly since 1957 averaging over 9 per cent annually. There is no plan to build a urea plant.

[Nitrogen, No. 31, (1964), 18-21]

### Ammonium Chloride

In view of the increasing world-wide demand for fertilizers in recent years the combined soda ash-ammonium chloride process is now attracting attention. The Central Glass Co. Ltd. of Japan has developed this process, which can be advantageously applied in producing compound fertilizers containing ammonium chloride.

In the conventional Solvay process of soda ash manufacture the utilization ratio of raw salt (NaCl) into soda ash is about 70 per cent, while the remaining 30 per cent of Na and the entire amount of Cl are wasted. In the combined process, these losses are lessened by transforming Cl into ammonium chloride. The mother liquor separated from the biocarbonate in the carbonator (carbonation of ammoniated brine) is sent to the ammonium chloride unit after ammonia has been absorbed to prevent the coprecipitation of sodium bicarbonate. The raw crushed salt, washed and purified, is added to the liquor and then cooled for the crystallization of ammonium chloride. The crystallized ammonium chloride is separated by the centrifuge and then granulated.

On the other hand, the mother liquor separated from ammonium chloride is sent into the carbonator.

The soda ash-ammonium chloride process has the following characteristics: (1) It is a complete recycle system in which soda ash and ammonium chloride are

produced in almost equivalent amounts; (2) almost all the sodium is converted into soda ash, while the entire amount of chloride is fixed by ammonia to ammonium chloride; (3) the amount of waste liquor discharged from the system is extremely small; (4) it dispenses with the large-scale distillation tower and lime kiln of the Solvay process.

This process has two types in Japan—one making crude ammonium chloride available in large-sized crystal, and the other which at first forms fine-sized crystals and then produces uniform-sized particles by using a granulator. The second type is known as Central Process.

[Look Japan, 10 (1965), 105, 2-4]

### New Design for Urea

Urea as a fertilizer is next to anhydrous ammonia with the highest nitrogen content. Effort to improve the quality and lower the production costs of urea has brought about many changes in urea processing. A new plant in Salamanca, in Mexico, owned by Fertilizantes del Bajío S. A., based on a process by the Swiss firm Lonza A. G. and designed and engineered by Lummus Co., has reached a capacity of 210 metric tons/day of urea.

The salient feature of Lonza-Lummus process is that all the unreacted CO<sub>2</sub> in the off-gases is absorbed by an ammonia-water solution in a primary absorber to form a carbonate solution which is returned to the reactor. The absorption conditions are carefully controlled to minimize the amount of water recycled. Operated under adiabatic conditions of about 390°F, the reactor is one of the smallest used in any process and achieves a very high conversion—up to 74 per cent—of CO<sub>2</sub> to urea. In addition to minimising design costs, this scheme reduces the steam requirements for carbonate decomposition and the load on the recycle system.

CO<sub>2</sub> entering the plant at 450 psig is compressed to about 4,300 psi in a 2-stage 360 hp. reciprocating compressor. Liquid ammonia, supplied at ambient temperature and about 280 psi., is mixed with recycled ammonia and boosted with a triplex pump to the reactor pressure. The NH<sub>3</sub>:CO<sub>2</sub> mole ratio in the reactor is maintained between 4.0:1 and 4.5:1. The reactor effluent, containing excess ammonia, unreacted carbamate, water and urea, then undergoes the following 3-stage purification sequence: (i) it passes into a primary decomposer where the pressure is reduced to 210-250

psi; most of the excess ammonia is flashed on reducing the pressure; (ii) the liquid after flashing is heated to decompose unreacted carbamate into ammonia and CO<sub>2</sub>. All these flashed off-gases are sent to the primary absorber and contacted against a counter-current flow of aqueous ammonia solution to recover all the CO<sub>2</sub> and a portion of NH<sub>3</sub> in the form of carbamate for recycle to the reactor. Operating the primary decomposer is advantageous because the ammonia that does not combine with CO<sub>2</sub> as carbamate in the recycle solution can later be condensed at the temperature of the cooling water available; (iii) the remaining aqueous phase, now mostly aqueous urea and some carbamate, is further depressurized and heated in the secondary decomposer at atmospheric pressure and in a flash tower kept under vacuum to achieve optimum recovery of NH<sub>3</sub> and CO<sub>2</sub>.

The last vacuum flash lowers the temperature of the urea solution to inhibit hydrolysis and biuret formation. The off-gases from the flash tower contain a large percentage of water, and direct condensation is possible. The dilute NH<sub>3</sub> flows to a secondary decomposer.

Urea solution is compressed to more than 99.5 per cent urea in a 2-stage evaporator, the second stage being of a rotary film-type.

[Chem. Engng., 72 (1965), 126-128]

### Demand for Naphtha

Only a few years ago naphtha was a surplus material. Though definitions vary, naphtha may be defined as embracing all light distillate above the kerosene range. Traditionally it is the raw material for high grade aviation and motor gasolines.

With the rapid growth in consumption of fuel oil and of middle distillates in Europe in the post-war era, the pattern of consumption of petroleum products changed, and the demand for gasolines fell while that of middle distillates increased. The problem of imbalance with which refiners in Europe and Japan were faced was aggravated by the large American imports of residual fuel oil and by the growing output of N. African crudes, with their high proportion of light ends.

One of the outlets of utilizing naphtha was town gas, especially in U. K. which has the most developed gas manufacturing techniques in Europe. To its traditional use of gas oil, the U.K. Gas Council added

growing purchases of refinery tail gases and l.p.g., and the growing availability of relatively cheap naphtha was a godsend. It quickly took advantage of ICI's steam-naphtha process, with later improvements, to convert increasing quantities of light disillate to town gas. Economically, plants using naphtha-based processes are attractive. The capital costs are relatively low, their thermal efficiency high and at the cost

price of naphtha they can turn out town gas at 6.5 *d* a therm or about half the cost of gas making by conventional coal carbonization.

A far more important outlet is provided by the chemical industry. Naphtha crackers are being installed in many countries to produce ethylene which forms the starting point for the manufacture of so many plastics and other products. The same

light distillate can be used in the production of acetylene, which is the base material for another important group of chemical products, aromatics, and ammonia for fertilizer production. The consumption of naphtha by the chemical and town gas industries of the western Europe and Japan is now running at an annual rate of over 14 million tons.

[Petr. Press Serv., 32 (1965), 129-130]



# News in Brief

## New Process for Phosphoric Acid

A new process for the production of phosphoric acid has been patented by the Dow Chemical Co. in the U.S.A. The process involves digestion of phosphate rock with hydrochloric acid followed by solvent extraction of the phosphoric acid from the calcium chloride solution. The extraction solvent used is a trialkylphosphate.

[Chem. Tr. J. 154 (1964), 4015, 732; Abstr. Res. & Indus., 9 (1964), 371]

## Ammonia in Coke Oven Gas

A method for the determination of ammonia in coke oven gas has been described in a Russian paper. The crude gas is first freed from mechanical impurities by passage through electrostatic and cotton wool filters and then passed through a coil in a thermostatic bath. An electrolytic cell containing a 0.3N solution of sulphuric acid and having two graphite electrodes is also immersed in the bath. High-frequency current is passed between the electrodes, and the electrical resistance of the solution is recorded. The resistance increases as ammonia is absorbed from the gas and the change in resistance is directly proportional to the amount of gas absorbed.

[Res. & Indus., 9 (1964), 381]

## New Gas Process

A new gas manufacturing process, known as the catalytic rich gas, has been developed recently by the Gas Council, U.K. It makes a methane-rich gas direct from light petroleum following on the gas recycle hydrogenator and non-catalytic, which was also invented the Council's Midland Research Station. A single basic process has been adapted to give a gas compatible with town gas as supplied today with the natural gas.

The process will meet the industry's present problem of enrichment to town gas standard of the lean, mainly hydrogen,

which will be produced by the many plants for steam reforming of naphtha, now under construction or planning. It can produce gas of 650-800 Btu/ft<sup>3</sup> after removal of carbon dioxide. Alternatively the gas can be partially reformed to make town gas in a single process direct from naphtha. The gas recycle hydrogenator will continue to have a place in areas where it is essential that gas should have the highest possible flame speed.

A nickel-ammonia catalyst is used to give the highest activity needed to carry out the reaction between steam and hydrocarbons at the relatively low temperature (500°-550°C)

[Fuel, 54 (1965), 82]

## NPK Compound Fertilizers

A freezing method has been developed for the production of NPK-1 compound fertilizer from apatite. The mineral is degraded by nitric acid, and from the solution calcium nitrate is separated by direct mixing with cooled petrol, which is then removed and recycled. The solution is then neutralized by gaseous ammonia using neutralization heat for partial concentration. Finally the product is partially converted to potassium salts, dried to a melt and granulated.

[Craha, M., Chem. Prum., 14 (1964), (4), 172-177; Abstr. NPKS Abstrs, 34 (1964), 6]

## Control of Cotton Rust

By application of heavy dressings of 60 per cent potash salts, the cotton rust could be first controlled and then suppressed completely. The first sign of potash deficiency in the cotton plant is a yellowish-white spotting of the leaves. In the large cotton-growing districts of the U.S.A. potash is applied in adequate quantities regularly in manuring, which removes the danger of attack by cotton rust.

[NPKS Abstr., 34 (1964), 7]

## Ammonium Sulphate Drying

A process has been developed whereby the ammonium sulphate is dried as it moves along a curved path by preheated air or fuel gas blown in at a tangent through jets inside the eddy chamber. The apparatus ensures a close contact between the material and the heat carrier, a high throughput and efficient drying of the product. The eddy drying chamber is a simple compact device. The plant operates reliably with throughputs of up to 4 tph, but drying units of this type can be designed for throughputs up to 10 tph and more.

[Shubeko, P. Z., et al Coke & Chem, U.S.S.R. 1963 (1), 35-37; Abstr. NPKS Abstr., 35 (1964), 5]

## Urea Prills

Urea prills of low biuret content are produced by providing a substantially anhydrous melt containing less than 0.5 per cent by weight of water and between 0.5 to 1.5 per cent by weight of biuret, the balance being urea. Treating said melt in a conversion zone maintained under an ammonia pressure between 10 and 100 atm at a temperature between 272° and 375°F for a time sufficient to achieve substantial equilibrium, a melt is obtained containing 0.1-0.5 per cent by weight of biuret and passing the low melt obtained to a prilling zone.

[M. W. Kellogg Co., NPKS Abstr., 36 (1964), 4]

## Ammonia for Preventing Corrosion

As a result of work carried out by the Central Electricity Generating Board, it has been decided that all Foster Wheeler boilers at the Bankside Generating Station of CEGB are to be equipped with ammonia injection system for preventing air-heater corrosion. In the short-term tests with ammonia injection, analysis of water used for washing the air-heaters showed that corrosion had been reduced by 73 per cent. Measurement with the air-cooled corrosion

probe indicated that corrosion is reduced by 89 per cent with ammonia injection.

[Nitrogen, (1965), 33, 36]

### Nitric Phosphate Fertilizers

In TVA's pilot plant work on the nitric phosphate process, several grades, viz. 15-15-15 and 20-20-0, have been produced at recycle ratios of 3 or less. Recycle ratios were lowered substantially using a pre-neutralizer to remove chemical heat and water from the process. The preneutralizer was effective in removing water from the slurry before ammoniation was completed. The slurry was fluid throughout and the loss of ammonia was 1 to 3 per cent over the range studied. The use of superphosphoric acid (76 per cent  $P_2O_5$ ) and highly concentrated nitric acid (65 per cent nitric acid) instead of the acids of normal concentrations should significantly decrease the recycle ratios.

In the current work, products with  $P_2O_5$  water solubilities of 25, 40 and 60 per cent have been satisfactorily produced. Usually the  $P_2O_5$  water solubility was varied by varying the proportion of ammonium phosphates. Products with N:  $P_2O_5$  ratios ranging from 2:1 to 1:2 have been satisfactorily produced, some of which include: 26-13-0, 20-10-10, 20-20-0, 15-15-15 14-28-0 and 10-20-20. Tests have been made

with sulphuric acid modification of the process to produce 14-14-0 grade, where preneutralizer was effective only in removing the heat of reaction since water had to be added to maintain slurry fluidity.

[Nitrogen, (1965), 33, 33-34]

### Potash

The world production of potash in 1963 increased by 12 per cent to about 10.4m. tonnes, the main contributory factors being the increased output in Canada, U.S.A. and U.S.S.R. The International Minerals and Chemical Corp. at Esterhazy (Canada) produced 732,000 short tons  $K_2O$  in the form of 60 per cent potassium muriate, U.S. potash industry raised its output by over 17 per cent, while potash production in U.S.S.R. was officially reported at 1,412,000 te of  $K_2O$ . While production in E. Germany has remained almost the same (1.75 m. tonnes), of which over 60 per cent was exported to the east European countries.

[Phosphorus & Potassium, No. 10, 1964, 27-28]

### Phosphoric Acids

A new product, 115 per cent  $H_3PO_4$ , offering a 95 per cent polyphosphoric

composition has been announced by Inorganic Chemicals Division of F.M.C. Corp. New York. It is a clear, viscous liquid, and tends to supercool. It is not corrosive as normal phosphoric acids. F.M.C.'s superphosphoric acid (105 per cent  $H_3PO_4$ ) and polyphosphoric acid (115 per cent  $H_3PO_4$ ) are equilibrium mixtures of orthophosphoric acid, pyrophosphoric acid and higher linear polyphosphoric acids.

[Phosphorus & Potassium, No. 12, 1964, 38-39]

Studies have been carried out by the TVA at Wilson Dam, Alabama (U.S.A.) for producing superphosphoric acid from wet process phosphoric acid. Rock phosphate when reacted with sulphuric acid produces an acid with 30 per cent  $P_2O_5$ , which is then concentrated in rubber-lined steel evaporators to about 54 per cent  $P_2O_5$ . Due to desirable properties exhibited by this acid at 70 per cent  $P_2O_5$  concentration—known at this concentration as superphosphoric acid. J. R. Simplot & Co. Idaho (U.S.A.) have developed a forced circulation vacuum evaporation process for concentrating the 54 per cent superphosphoric acid for producing 70-72 per cent  $P_2O_5$ .

[Chem. Engr. Prog., 60 (1964), 7, 97-99]



# STATISTICS

TABLE 1—STATE-WISE DISTRIBUTION OF MURIATE OF POTASH (1964)

(metric tonnes)

State	January to March 1964	April to June 1964	July to Sept. 1964	Oct. to Dec. 1964	1964 (Jan. to Dec.)
Andhra Pradesh	1,137	664	1,068	653	3,522
Assam	3	706	333	381	1,423
Bihar	836	2,002	1,298	1,738	5,874
Gujarat	340	859	1,102	859	3,160
Jammu & Kashmir	—	—	1	1	2
Kerala	3,433	4,871	7,087	5,016	20,407
Madhya Pradesh	5	22	1	1	29
Madras	5,214	4,514	4,680	8,151	22,559
Maharashtra	3,887	2,995	2,268	3,034	12,184
Mysore	3,500	3,406	2,909	3,389	13,204
Orissa	110	385	377	182	1,054
Punjab	45	28	316	1,185	1,574
Rajasthan	—	1	137	5	143
Uttar Pradesh	22	320	50	8	400
West Bengal	691	326	3,912	5,893	10,822
Himachal Pradesh	—	—	1	70	71
Goa	—	—	10	—	10
Total	19,223	21,099	25,550	30,566	96,438

Source: Indian Potash Supply Agency Ltd., Madras.

[FAI Inf. Serv., 6 (1965), 5, 6]

TABLE 2—AVERAGE ANNUAL RATES OF GROWTH IN THE CONSUMPTION OF PLANT NUTRIENTS 1953/54-1960/61

	Average Annual Rate of Growth in Consumption 1953/54-1960/61		
	N	(Per cent) P <sub>2</sub> O <sub>5</sub>	K <sub>2</sub> O
World	8.9	5.4	5.7
ECAFE region	7.8	6.8	9.3
Australia	7.6	3.9	9.6
Burma	33.1	56.4	—
Cambodia	—	—	—
Ceylon	7.0	1.5	0.5
China: Taiwan	6.8	5.1	20.0
Federation of Malaya	18.4	36.5	23.4
Hong Kong	2.2	—	—
India	13.4	19.2	20.3
Indonesia	8.2	12.0	19.9
Iran	111.6	63.4	46.8
Japan	4.9	10.7	7.7
Korea, Republic of	7.5	23.4	5.0
New Zealand	0.6	0.2	16.5
North Borneo	43.9	62.4	70.3
Pakistan	28.6	128.1	101.9
Philippines	9.1	—	18.8
Singapore	14.4	14.1	26.8
Thailand	—	—	—
Viet-Nam	30.4	7.0	28.3

[Chemical Age of India, 15 (1964), 3, 282]

TABLE 3—ANNUAL RATES OF GROWTH IN THE OUTPUT  
OF PLANT NUTRIENTS (1953/54-1960/61)

	(Per cent)		
	N	P <sub>2</sub> O <sub>5</sub>	K <sub>2</sub> O
World	9.7	6.3	6.5
ECAFE region	8.6	7.7	—
Australia	6.6	5.4	—
China: Taiwan	18.9	20.3	—
India	5.7	21.0	—
Japan	8.3	9.9	—
New Zealand	1.4	5.4	—
Pakistan	12.0 <sup>1</sup>	24.9 <sup>2</sup>	—
Philippines	21.4	—	—

<sup>1</sup> 1957/58-1960/61

<sup>2</sup> 1956/57-1960/61

[Chemical Age of India, 15 (1964), 3, 283]

TABLE 4—CONSUMPTION RATIOS OF PLANT NUTRIENTS  
(1953/54-1955/56) AND (1958/59-1960/61)

	1953/54-1955/56			1958/59-1960/61		
	N	P <sub>2</sub> O <sub>5</sub>	K <sub>2</sub> O	N	P <sub>2</sub> O <sub>5</sub>	K <sub>2</sub> O
World	1	1.2	1.02	1	1.02	0.88
Europe	1	1.27	1.31	1	0.89	1.09
North and Central America	1	1.18	0.92	1	0.98	0.77
ECAFE region	1	1.05	0.49	1	1	0.52
Australia	1	21.9	0.88	1	18.5	0.97
Burma	1	0.15	0.01	1	0.35	—
Cambodia	—	—	—	1	0.308	.29
Ceylon	1	0.09	1	1	0.07	.74
China (Taiwan)	1	0.37	0.16	1	0.34	.29
Federation of Malaya	1	0.13	0.35	1	0.27	.44
Hong Kong	1	0.03	0.02	—	—	—
India	1	0.14	0.08	1	0.19	.11
Indonesia	1	0.25	0.14	1	0.3	.23
Iran	1	2.79	1.08	1	0.77	.17
Japan	1	0.5	0.68	1	0.66	.78
Korea, Republic of	1	0.28	0.04	1	0.55	.03
New Zealand	1	34.3	4	1	34	8.4
North Borneo	1	0.5	0.57	1	0.92	1.31
Pakistan	1	0.01	0.01	1	0.18	0.08
Philippines	1	0.63	0.3	1	0.35	0.46
Singapore	1	0.17	0.34	1	0.17	0.56
Thailand	—	—	—	1	0.49	0.26
Viet-Nam, Republic of	1	0.27	0.18	1	0.10	0.17

[Chemical Age of India, 15 (1964), 3, 286]

TABLE 5—OUTPUT RATIOS OF PLANT NUTRIENTS

	Ratio of Plant Nutrients Produced					
	1953/54			1960/61		
	N	P <sub>2</sub> O <sub>5</sub>	K <sub>2</sub> O	N	P <sub>2</sub> O <sub>5</sub>	K <sub>2</sub> O
World	1	1.19	1.01	1	0.95	0.82
ECAFE region	1	1.21	—	1	1.15	—
ECAFE region (ex- cluding Australia and New Zealand)	—	—	—	1	0.52	—
Australia	1	26	—	1	24	—
China: Taiwan	1	1.12	—	1	2.25	—
India	1	0.21	—	1	0.54	—
Japan	1	0.45	—	1	0.5	—
New Zealand	1	50	—	1	66	—
Pakistan	1	0.06 <sup>1</sup>	—	1	1.27	—
Philippines	1	0.12 <sup>2</sup>	—	1	—	—

<sup>1</sup> 1957/58

<sup>2</sup> 1957/58

[Chemical Age of India, 15 (1964), 3, 284]

TABLE 6—PERCENTAGE SHARE OF ECAFE COUNTRIES  
IN THE REGION'S OUTPUT OF FERTILIZERS (1953/54  
AND 1960/61)

	Nitrogenous (N) fertilizers		Phosphatic (P <sub>2</sub> O <sub>5</sub> ) fertilizers	
	1953/54	1960/61	1953/54	1960/61
Australia	2.2	1.9	47.0	40.3
China: Taiwan	2.2	4.1	2	4.4
India	9.4	7.8	1.6	3.7
Japan	85.0	83.4	31.6	36.2
New Zealand	0.5	0.3	17.8	15.3
Pakistan	—	0.8	—	0.1
Philippines	0.9	1.9	—	—

[Chemical Age of India, 15 (1964), 3, 284]



TABLE 7—ECAFE COUNTRIES: DOMESTIC OUTPUT IN RELATION TO DOMESTIC CONSUMPTION OF NITROGENOUS FERTILIZERS (1953/54-1960/61)

(Domestic output as per cent of consumption in terms of N)

Country	1953/54	1954/55	1955/56	1956/57	1957/58	1958/59	1959/60	1960/61
Australia .. .. .	88.7	68.7	87.5	77.9	70.2	72.1	93.8	94.0
Burma .. .. .	—	—	—	—	—	—	—	—
Cambodia .. .. .	—	—	—	—	—	—	—	—
Ceylon .. .. .	—	—	—	—	—	—	—	—
China: Taiwan .. .. .	23.2	16.8	22.8	21.3	20.3	30.9	35.3	48.4
Federation of Malaya .. .. .	—	—	—	—	—	—	—	—
Hong Kong .. .. .	—	—	—	—	—	—	—	—
India .. .. .	77.0	71.0	57.6	49.0	45.3	39.4	34.9	44.8
Indonesia .. .. .	—	—	—	—	—	—	—	—
Iran .. .. .	—	—	—	—	—	—	—	—
Japan .. .. .	121.9	121.2	121.2	132.2	140.3	144.9	158.0	137.0
Korea, Republic of .. .. .	—	—	—	—	—	—	—	—
New Zealand .. .. .	69.6	45.8	46.9	56.4	58.2	62.0	56.6	51.6
North Borneo .. .. .	—	—	—	—	—	—	—	—
Pakistan .. .. .	—	—	—	—	70.0	75.6	34.3	14.9
Philippines .. .. .	—	51.9	—	61.6	54.4	69.6	—	—
Singapore .. .. .	—	—	—	—	—	—	—	—
Thailand .. .. .	—	—	—	—	—	—	—	—
Viet-Nam, Republic of .. .. .	—	—	—	—	—	—	—	—
ECAFE region .. .. .	86.7	79.5	79.3	78.6	84.9	87.6	83.6	96.5

[Chemical Age of India, 15 (1964), 3, 285]

TABLE 8—ECAFE COUNTRIES: DOMESTIC OUTPUT IN RELATION TO DOMESTIC CONSUMPTION OF PHOSPHATE FERTILIZERS (1953/54-1960/61)

(Domestic output as per cent of consumption in terms of  $P_2O_5$ )

Country	1953-54	1954-55	1955-56	1956-57	1957-58	1958-59	1959-60	1960-61
Australia .. .. .	100	100.1	100.1	100	100.1	97.7	99.8	99.6
Burma* .. .. .	38.5	2000	500	—	—	—	—	—
Ceylon* .. .. .	11.4	15.6	16.7	8.6	11.4	9.3	—	—
China: Taiwan .. .. .	68.2	49.3	72.4	70.1	60.8	65.4	78.4	76.0
India .. .. .	66.2	—	99.4	99.3	98.3	98.2	100	99.8
Japan .. .. .	126.8	119.0	116.0	114.8	110.2	106.9	104.8	104.6
Korea, Republic of .. .. .	1.5	0.4	—	—	—	—	—	—
New Zealand .. .. .	91.4	89.9	93	95.1	94.7	94.7	97.8	98.2
Pakistan .. .. .	—	—	—	20	100	100	6.3	8.8
Philippines .. .. .	—	—	—	—	2.4	84.7	—	—
ECAFE region .. .. .	100	96	98	106	92	96	92	100

\* Output in organics.

[Chemical Age of India, 15 (1964), 3, 286]



TABLE 9—NUTRIENT CONTENTS OF FERTILIZERS

Material	Total nitrogen	Total phosphorus pentoxide $P_2O_5$	Available phosphorus pentoxide $P_2O_5$	Water soluble phosphorus pentoxide $P_2O_5$	Water soluble potash	Total lime CaO	Equi- valent acidity	Equi- valent basicity
(per cent)								
<i>Nitrogenous materials</i>								
1. Ammonia anhydrous ..	82.0	—	—	—	—	—	—	—
*2. Ammonium chloride ..	25.0**	—	—	—	—	—	148	—
3. Ammonium nitrate ..	33.5	—	—	—	—	—	128	—
*4. Ammonium sulphate ..	20.6**	—	—	—	—	—	60	—
*5. Ammonium sulphate nitrate ..	26.0**	—	—	—	—	—	110	—
*6. Calcium ammonium nitrate ..	20.5**	—	—	—	—	—	93	—
7. Calcium cyanamide ..	21.0	—	—	—	—	10.0–20.0	0	—
†8. Sodium nitrate ..	16.0**	—	—	—	—	54.0	0	63
*9. Urea ..	44.0**	—	—	—	—	—	—	29
10. Urea formaldehyde compound ..	38.0	—	—	—	—	—	80	—
							68	—
<i>Phosphorus materials</i>								
11. Basic slag Bessemer ..	—	15.0–18.0	13.5–16.5	—	—	45.0–50.0	—	Basic
12. Dicalcium phosphate ..	—	—	34.0**	—	—	32	—	25
13. Phosphoric acid ..	—	54.0	54.5	54.0	—	—	Acidic	—
*14. Single superphosphate:								
Grade I ..	—	—	20.5**	20.0**	—	—	0	0
Grade II ..	—	—	18.5**	18.0**	—	—	0	0
Grade III ..	—	—	16.5**	16.0**	—	—	0	0
15. Triple superphosphate ..	—	—	—	40.0**	—	—	0	0
16. Kotka phosphate ..	—	25.0**	16.0**	8.0**	—	—	0	0
<i>Potassium materials</i>								
17. Kainite including carnalite and silvinit ..	—	—	—	—	10.0–20.0	0.5–5.0	0	0
18. Potash from wood-ash ..	—	—	—	—	51.0	No data	—	Basic
19. Potassium chloride (muriate of potash) ..	—	—	—	—	60.0**	—	—	—
20. Potassium sulphate (sulphate of potash) ..	—	—	—	—	48.0**	—	—	—
<i>Nitrogen-Phosphorus materials</i>								
21. Ammoniated superphosphate (Ordinary) ..	2.0–5.0	14.0–20.0	13.0–19.0	—	—	23.0–29.0	4.7	—
22. Ammoniated superphosphate (Double) ..	4.0–6.0	40.0–49.0	38.0–48.0	—	—	16.5–22.5	11–14	—
23. Diammonium phosphate ..	21.0**	—	—	53.0**	—	—	77	—
24. Mono-ammonium phosphate ..	11.0**	—	—	48.0**	—	—	55	—
25. Ammonium phosphate sulphate ..	16.0**	—	—	20.0**	—	—	86	—
*26. Nitrophosphate ..	12.9	—	12.9	—	—	—	—	—
<i>Nitrogen-Phosphorus-Potassium materials</i>								
27. Ammonium potassium phosphate ..	5.5	54.0	54.0	—	18.5	—	Acidic	—
28. Nitrophoska ..	13.0	13.5	13.0	—	21.0	9.0	Acidic	—

Sources: (i) \*\* Fertiliser (Control) Order, 1957.

(ii) Efficient Use of Fertilisers—F.A.O. Agricultural Studies No. 43.

\* Fertilisers manufactured in India.

† Fertilisers imported in India.

Production of 20-20-0 grade of mono-ammonium sulphate with urea and 20-20-0 grade of ammonium phosphate sulphate with diammonium phosphate and ammonium sulphate has also been planned in India.

Equivalent acidity is the number of parts by weight of calcium carbonate ( $CaCO_3$ ) required to neutralise the acidity resulting from the use of 100 parts of the fertiliser material.

Equivalent basicity is the number of parts by weight of calcium carbonate ( $CaCO_3$ ) that corresponds in acid neutralising power of 100 parts of the fertiliser material.

[Fertilizer Statistics 1963-64, (Fert. Assn. of India, New Delhi), 1965, 156-157]



TABLE 10—AVERAGE CHEMICAL COMPOSITION OF SOME ORGANIC MANURES, %

Material	N	P <sub>2</sub> O <sub>5</sub>	K <sub>2</sub> O
I. Bulky organic manures			
Farmyard manure .. .. .	0.5–1.5	0.4–0.8	0.5–1.9
Compost (urban) .. .. .	1.2–2.0	1.0	1.5
Compost (rural) .. .. .	0.4–0.8	0.3–0.6	0.7–1.0
Green manures (various average) .. .. .	0.5–0.7	0.1–0.2	0.8–1.6
II. Oil cakes			
(a) Non-edible cakes			
Castor cake .. .. .	5.5–5.8	1.8–1.9	1.0–1.1
Cotton seed cake (undecorticated) .. .. .	3.9–4.0	1.8–1.9	1.6–1.7
Mahua cake .. .. .	2.5–2.6	0.8–0.9	1.8–1.9
Karanj Cake .. .. .	3.9–4.0	0.9–1.0	1.3–1.4
Neem cake .. .. .	5.2–5.3	1.0–1.1	1.4–1.5
Safflower cake (undecorticated) .. .. .	4.8–4.9	1.4–1.5	1.2–1.3
(b) Edible oil cakes			
Coconut cake .. .. .	3.0–3.2	1.8–1.9	1.7–1.8
Cotton seed cake (decorticated) .. .. .	6.4–6.5	2.8–2.9	2.1–2.2
Groundnut cake .. .. .	7.0–7.2	1.5–1.6	1.3–1.4
Jambo cake .. .. .	4.9–5.0	1.6–1.7	1.8–1.9
Linseed cake .. .. .	5.5–5.6	1.4–1.5	1.2–1.3
Niger cake .. .. .	4.7–4.8	1.8–1.9	1.3–1.4
Rapeseed cake .. .. .	5.1–5.2	1.8–1.9	1.1–1.2
Safflower cake (decorticated) .. .. .	7.8–7.9	2.2–2.3	1.9–2.0
Sesamum or til cake .. .. .	6.2–6.3	2.0–2.1	1.2–1.3
III. Manures of animal origin			
Dried blood .. .. .	10–12	1.0–1.5	0.6–0.8
Fish manure .. .. .	4–10	3–9	0.3–1.5
Bird guano .. .. .	7–8	11–14	2–3
Bone meal (raw) .. .. .	3–4	20–25	—
Bone meal (steamed) .. .. .	1.0–2.0	25–30	—
Activated sludge (dry) .. .. .	5–6	3–3.5	0.5–0.7
Settled sludge (dry) .. .. .	2–2.5	1–1.2	0.4–0.5
Night soil .. .. .	1.2–1.5	0.8–1.0	0.4–0.5
Cattle dung and urine mixed .. .. .	0.60	0.15	0.45
Horse dung and urine mixed .. .. .	0.70	0.25	0.55
Sheep dung and urine mixed .. .. .	0.95	0.35	1.00
Human urine .. .. .	1.0–1.2	0.1–0.2	0.2–0.3

[Fertilizer Statistics 1963-64, (Fert. Assn of India, New Delhi), 1965, 160-161]